# Fundamentals of Pulsed Plasmas for Materials Processing

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# Outline

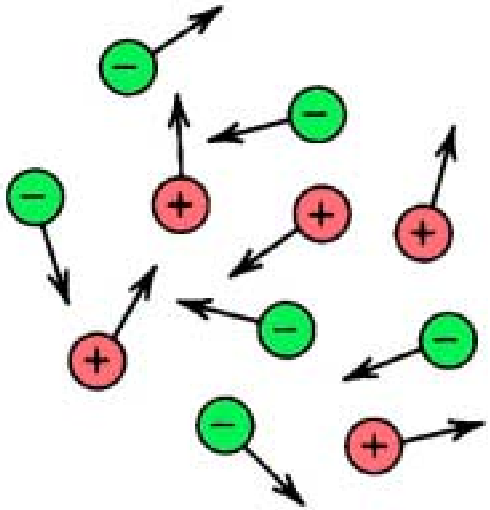
- Plasma
- Sheaths
- Dimensionless parameters
- *Pulsed* plasmas and sheaths
- Selected examples of pulsed plasma processing:
  - Plasma Immersion Ion Processing (PIIP, pulsed CVD)
  - Pulsed filtered arc deposition, and MePIIID
  - Pulsed magnetron sputtering

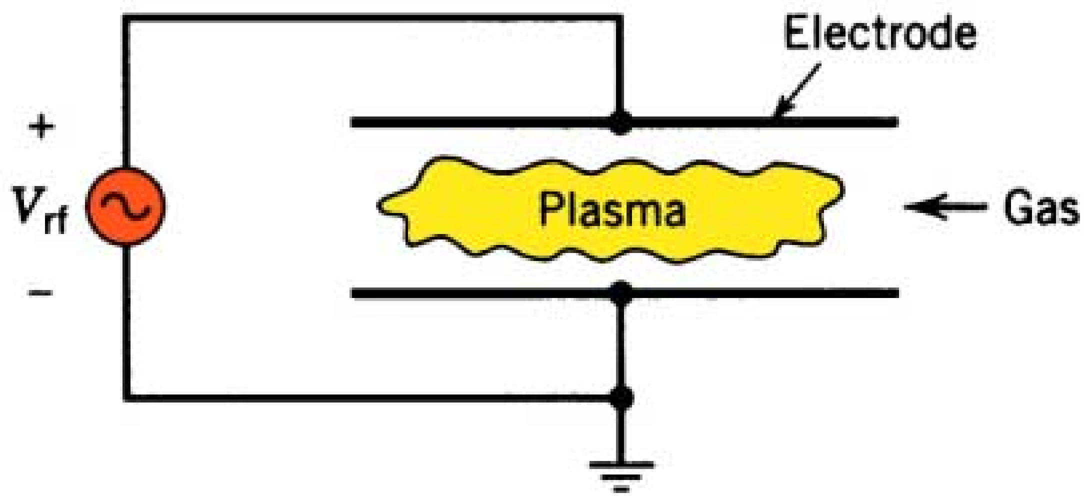
This talk is a mixture of tutorial, review, and original research paper.

# Pulsed Plasmas

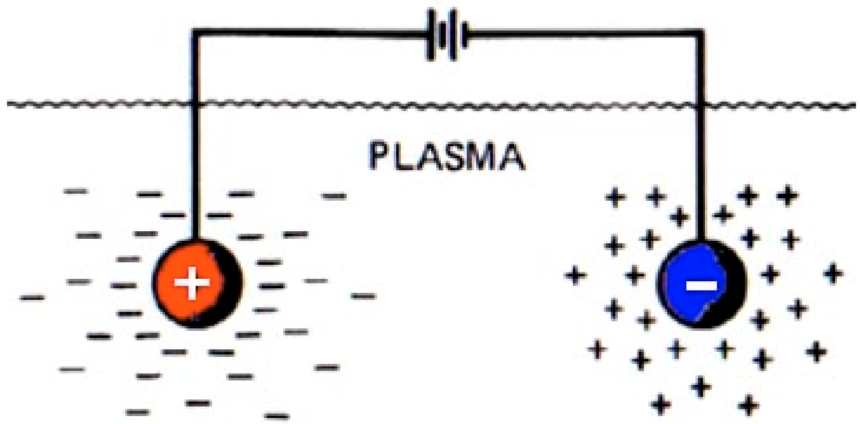
# Plasma

- 4th state of matter
- ensemble of charged particles with collective behavior
- in the lab generated by some sort of discharge





# Characteristic Parameters of Plasmas




Debye length

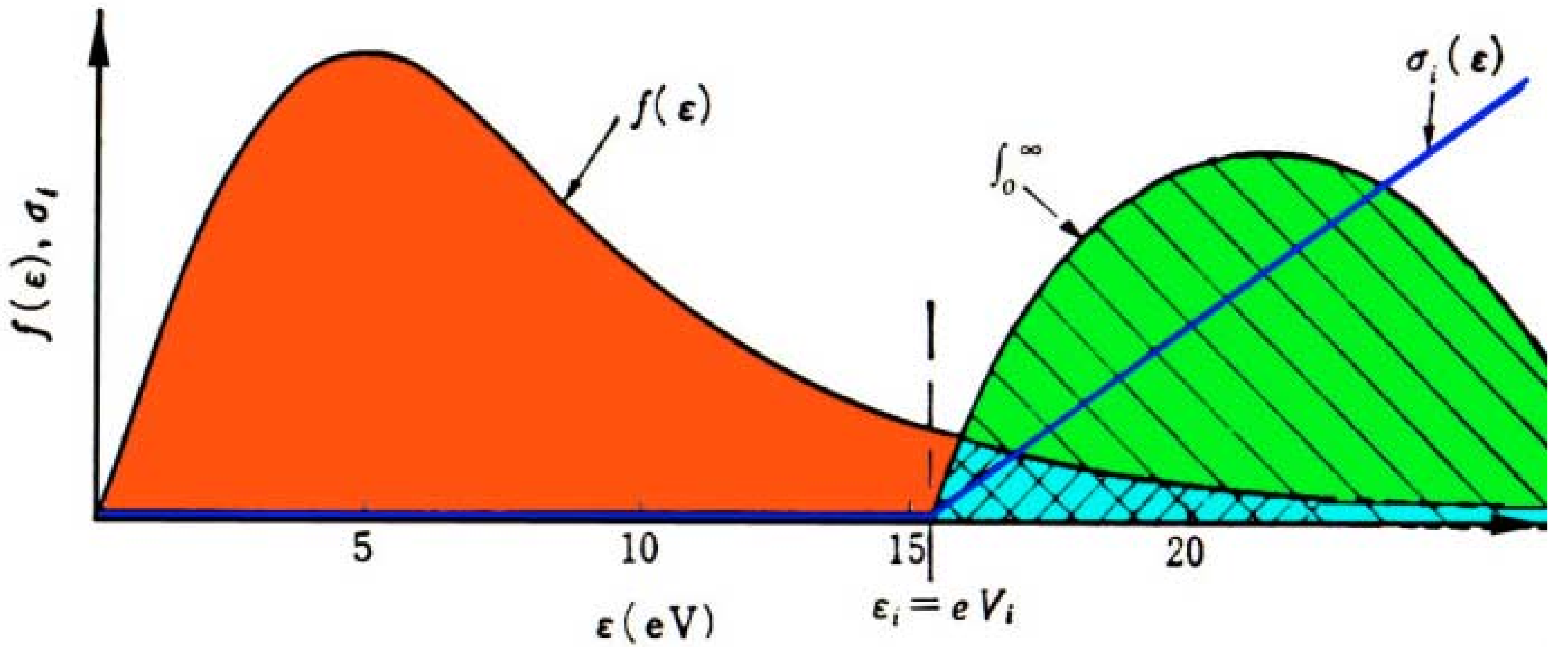
$$\lambda_{De} = \left( \frac{\varepsilon_0 k T_e}{n_e e^2} \right)^{1/2}$$

Plasma frequency

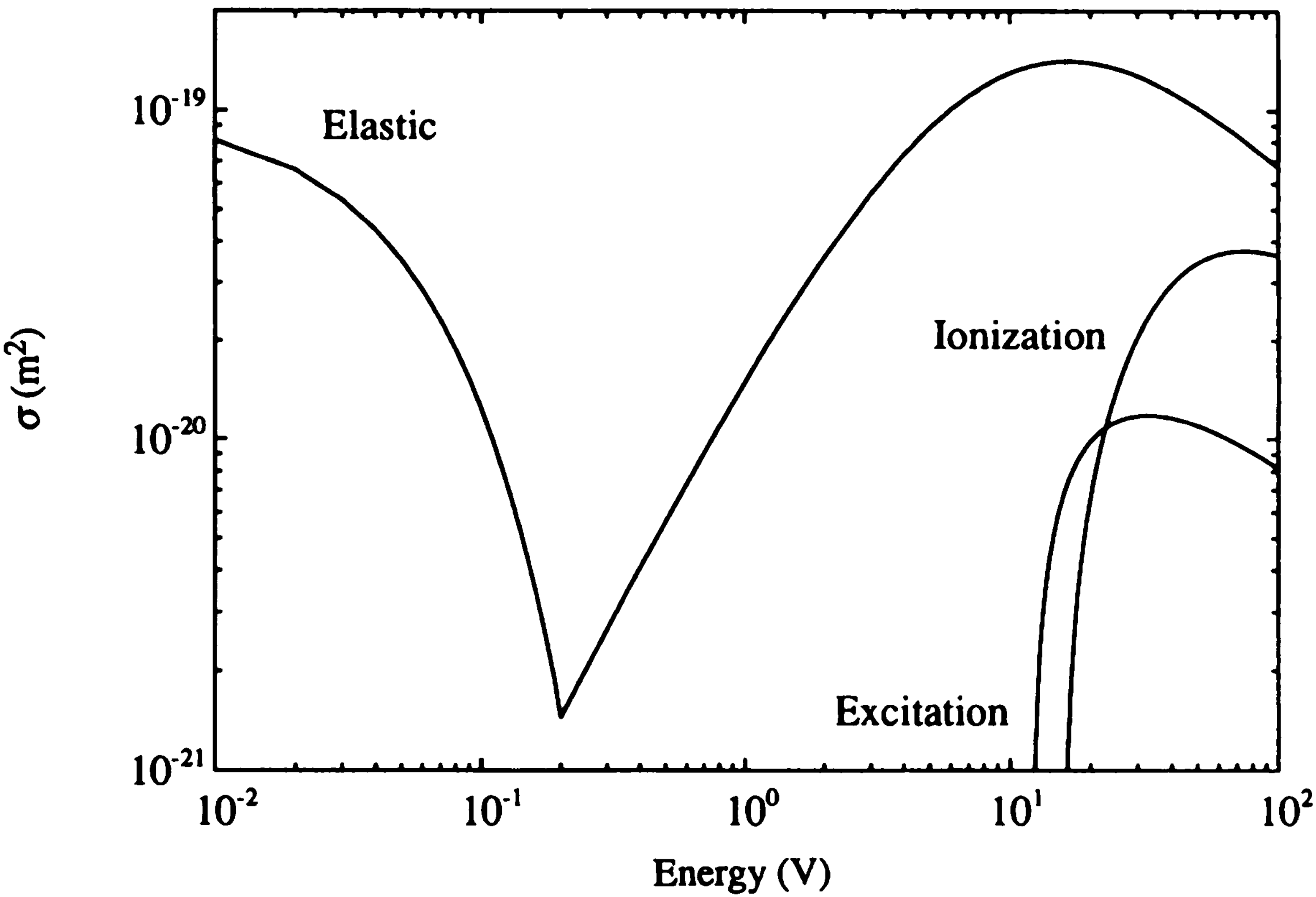
$$\omega_{pl,e} = \left( \frac{n_e e^2}{\varepsilon_0 m_e} \right)^{1/2}$$

# Distribution Functions and Rate Coefficients

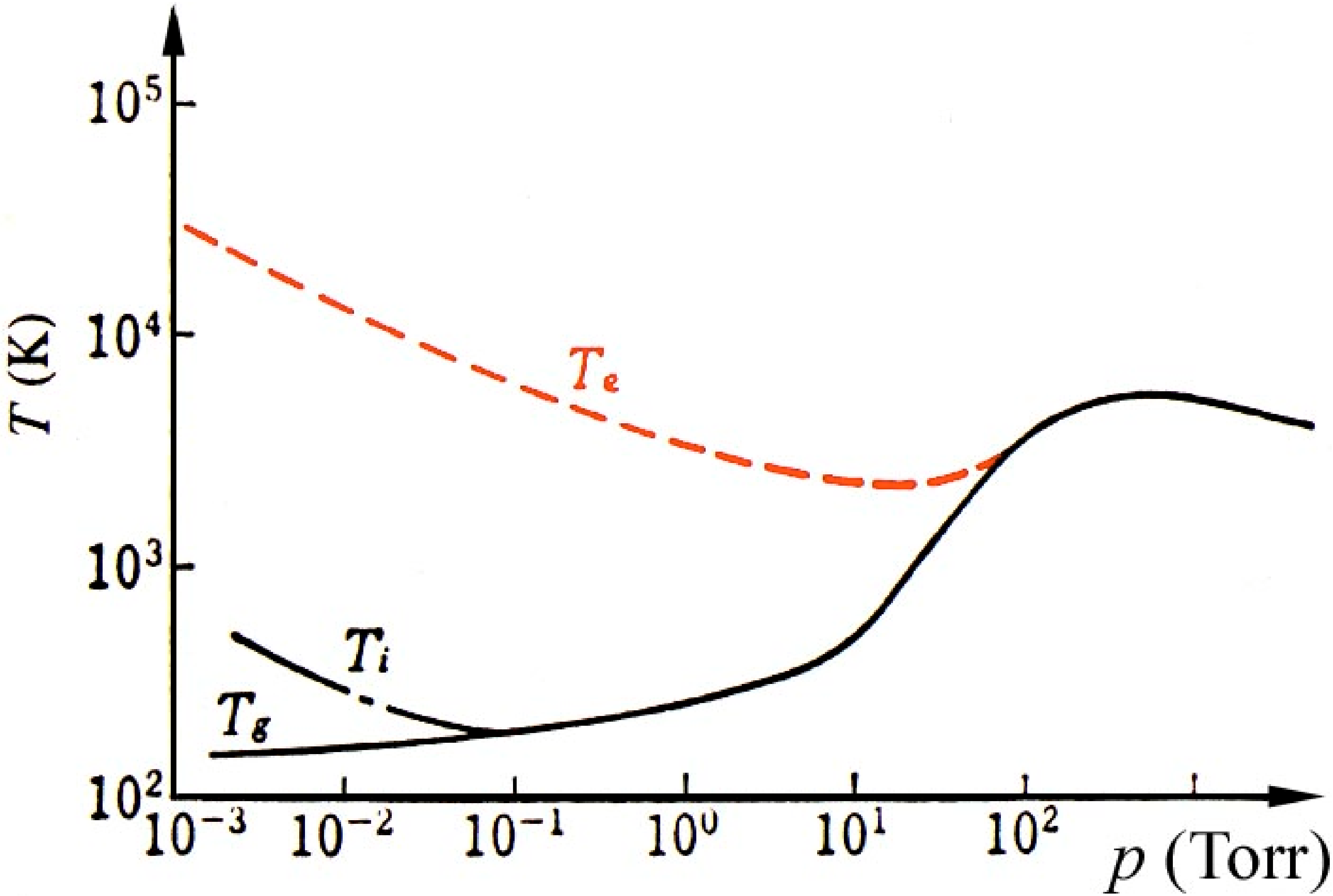
Mean free path $$\lambda_\alpha = \left( \sum_\beta n_\beta \sigma_{\alpha\beta} \right)^{-1}$$



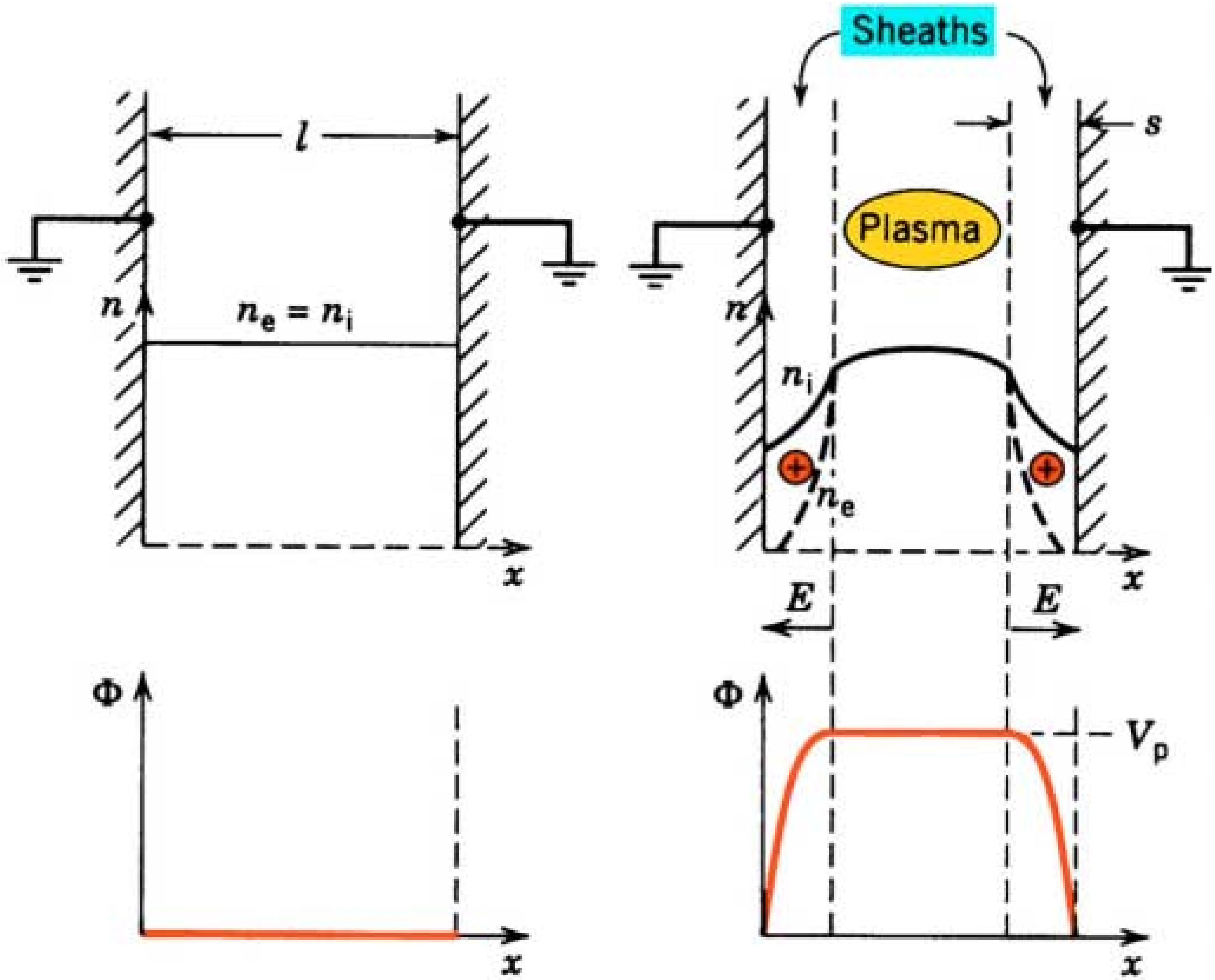
# Collisions in Plasmas



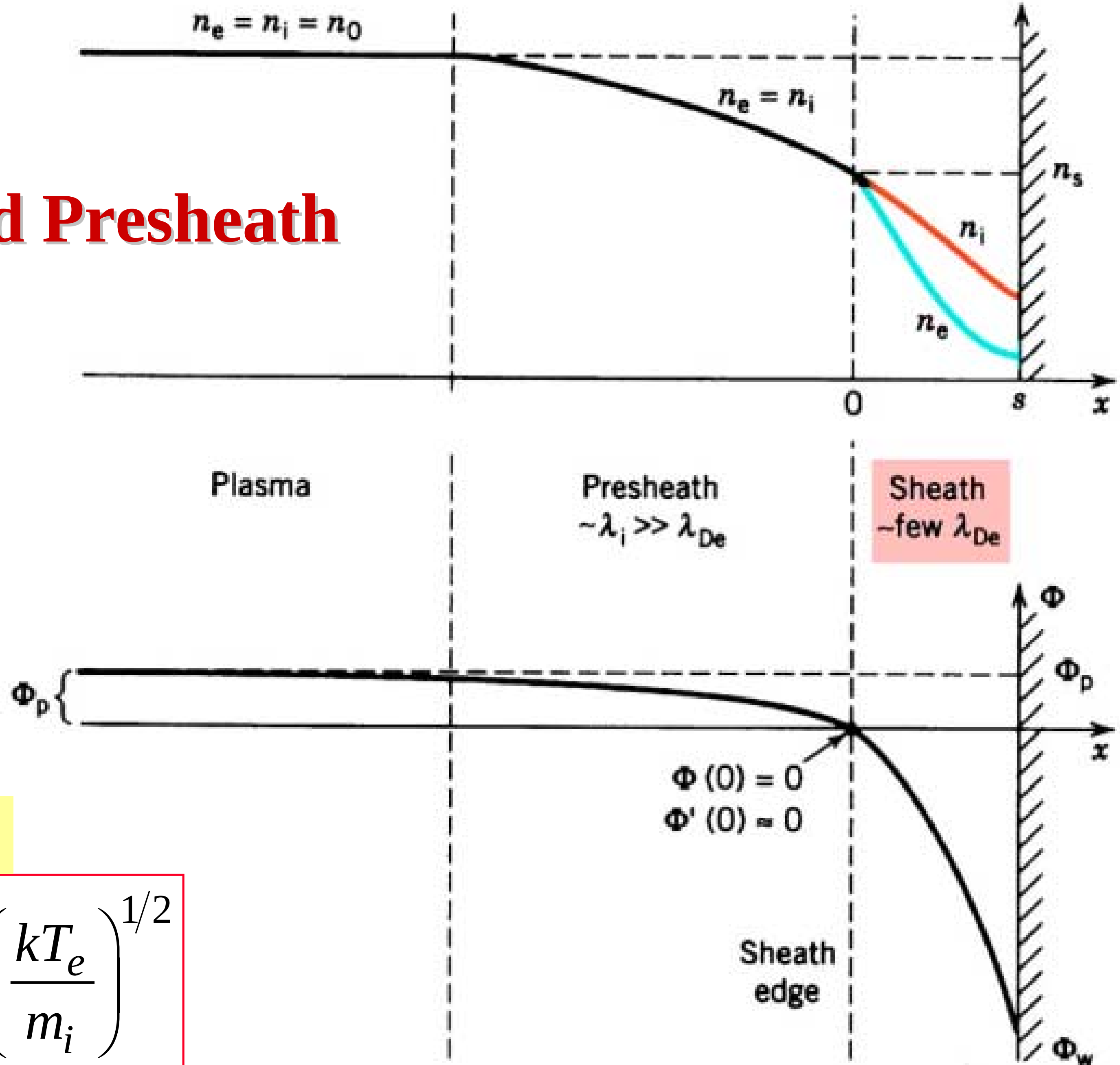
# Temperature (Non-)Equilibrium



# Plasma and Sheaths



# Sheaths and Presheath




Bohm velocity

$$u_{is} = u_{Bohm} = \left(\frac{kT_e}{m_i}\right)^{1/2}$$

# Re-interpretation of Child Law (1911) for Plasma Sheath

Poisson equation

$$\boxed{\varepsilon_0 \nabla \bullet \mathbf{E} = \rho}$$

Space charge limited current

self-adjusting sheath
(Child Sheath)

Child current

$$\boxed{j_i = \frac{4}{9}\varepsilon_0 \left(\frac{2e}{m_i}\right)^{1/2} \frac{V_0^{3/2}}{s^2}}$$

$$\boxed{s_{Child} = \frac{\sqrt{2}}{3}\lambda_{De}\left(\frac{2eV_0}{kT_e}\right)^{3/4}}$$

# Dimensionless Parameters

$$\text{dimensionless parameter} = \frac{\text{quantity of unit } X}{\text{characteristic parameter of unit } X}$$

- Examples:
  - degree of ionization $\alpha = \dfrac{n_i}{n_i + n_0}$
  - duty cycle $\delta = \dfrac{t_{on}}{t_{on} + t_{off}}$
  - Knudsen number $Kn = \lambda / \ell$
  - pulse rise parameter $\tau_{rise} = t_{rise}\,\omega_{pl,i}$

# Dimensionless Parameters

- Advantage of using dimensionless parameters:

In a *dynamic* situation, usually both the normalized and the normalizing quantities change. The elegance and power of dimensionless parameters is to be able to immediately evaluate a physical situation.

- Example:
  - collisionality in the sheath region = $\dfrac{\text{mean free path}}{\text{sheath thickness}}$

# *Pulsed* Plasmas

- When pulses are applied: new set of parameters or "control knobs" appear:
  - pulse duration
  - duty cycle
  - pulse amplitude

$$\delta = \frac{t_{on}}{t_{on} + t_{off}}$$

- distinction between average and pulse parameters
- extreme plasma parameters are possible during pulses
- process can have momentary high power, leading to more energetic and ionized particles in plasma

***Energetic Condensation***

# Energetic Relation Between Implantation and Deposition Processes

*Ion Energy*

Implantation

*Film growth is still possible for low duty cycle of bias*

sputter yield = 1 for $E_i$=300-1200 eV

Subplantation

Deposition

Ion plating, MePIIID

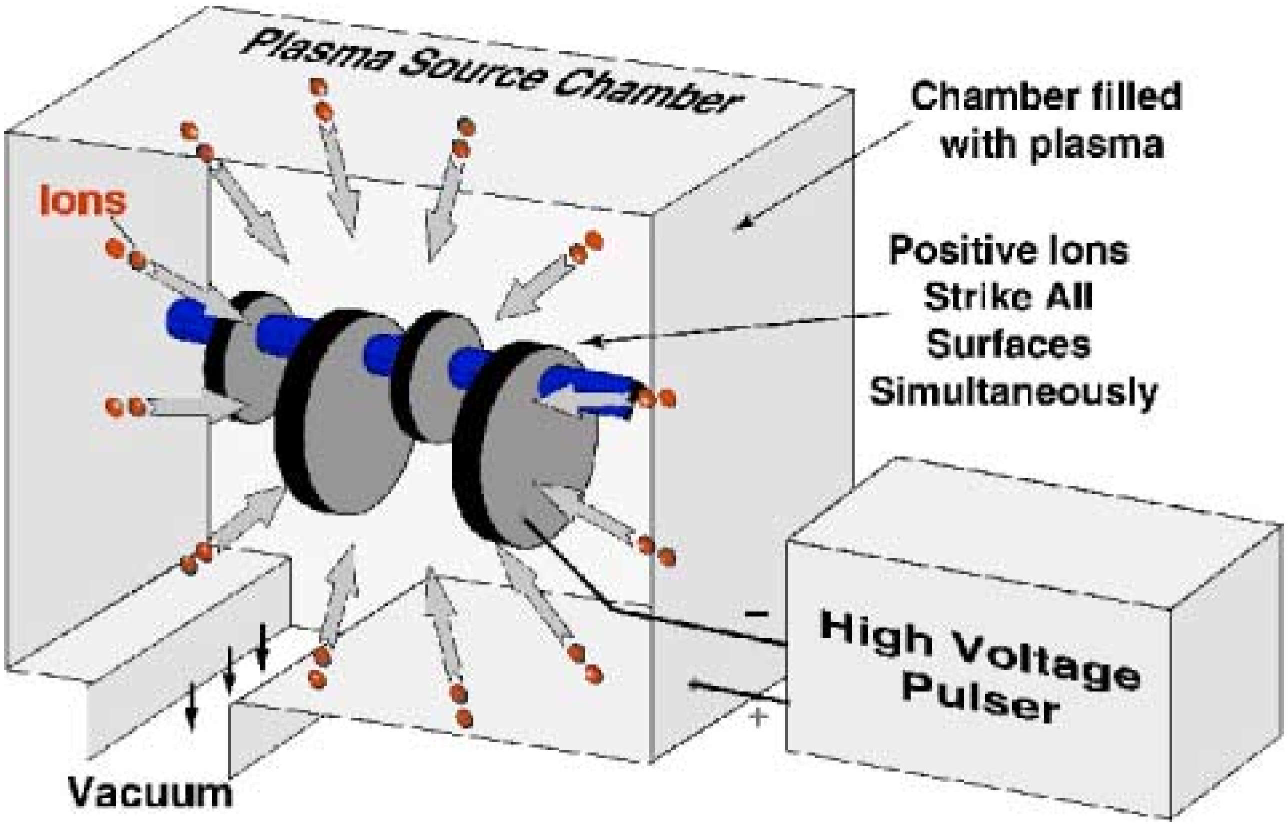
cathodic arc deposition

sputtering

evaporation

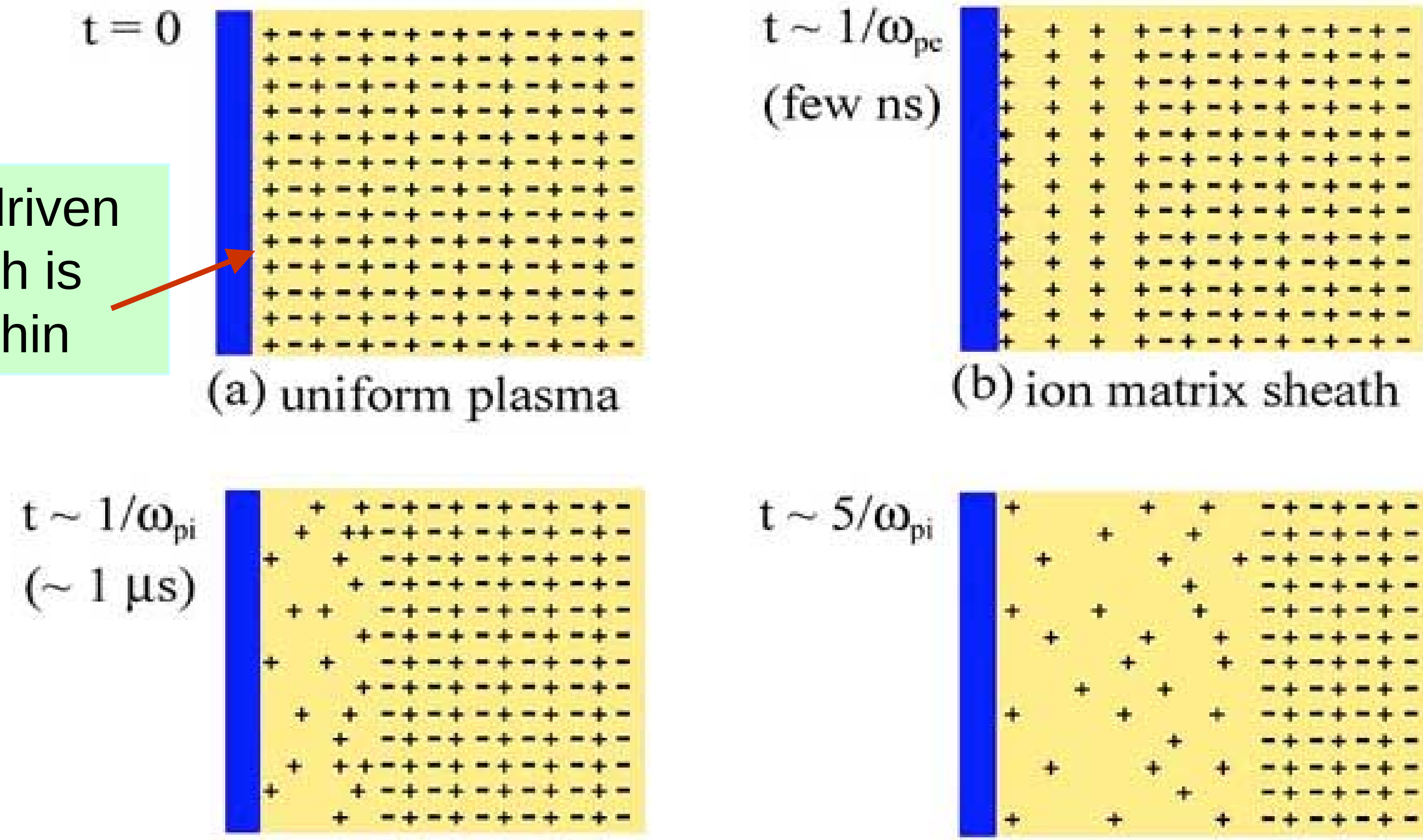
# Transient Sheath

- Resource:  PIII theory.
- conformal ion implantation of plasma ions by acceleration in high voltage sheath



# Sheath Development

non-driven sheath is very thin




Application of dimensionless parameters:

Ion matrix sheath exists only if $\tau_{rise} = t_{rise}\,\omega_{pl,i} < 1$

# Sheath Development

• If pulse rise is slow: $\tau_{rise} = t_{rise}\omega_{pl,i} > 1$

Ion matrix sheath does not exist but time-dependent Child sheath.

Examples of dimensionless parameters

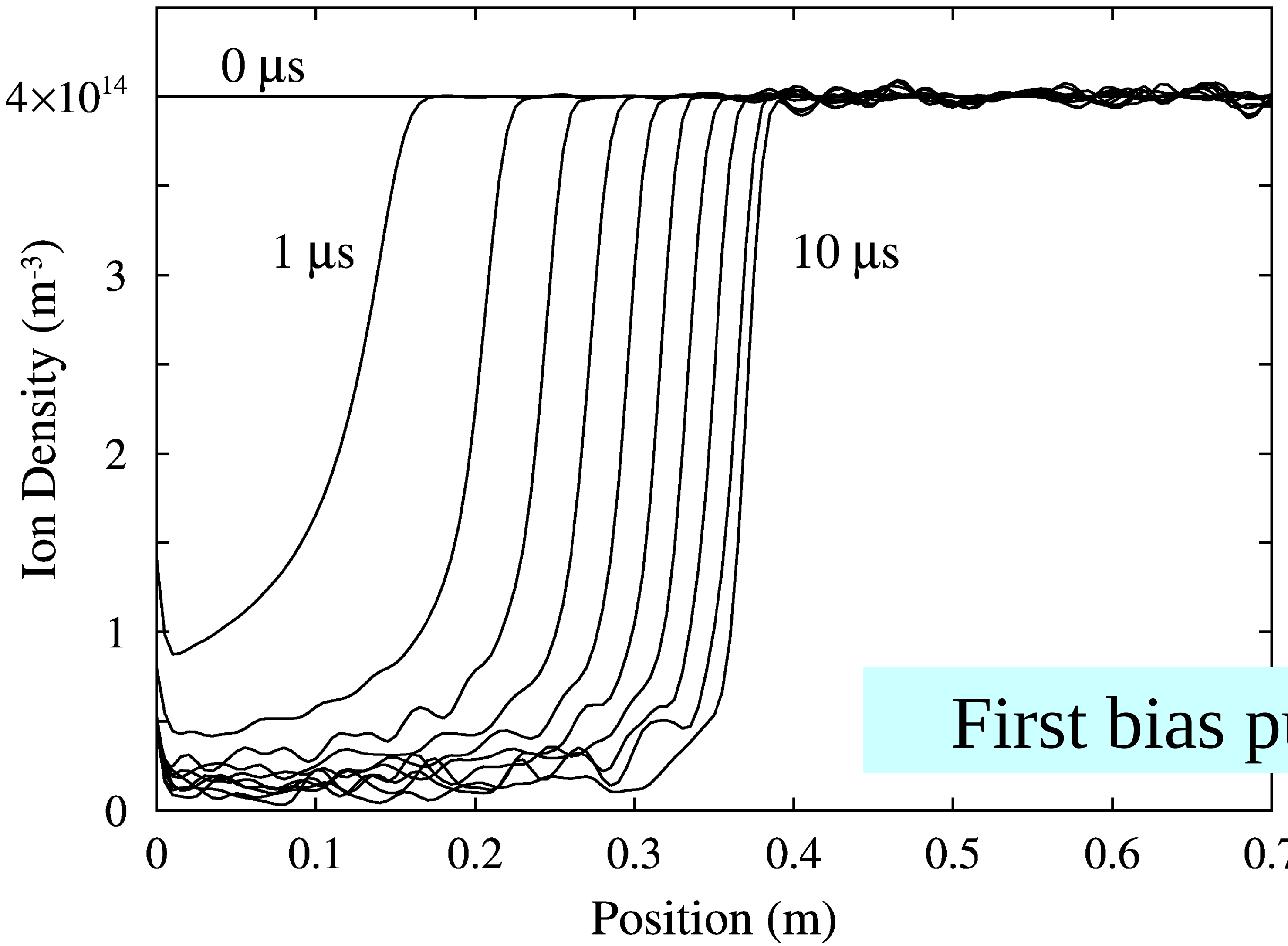
• If pulse sequence is fast $\tau_{off} = t_{off} / t_{restore} < 1$

where $t_{restore} \approx \dfrac{s_{Child}^2}{D_{ambi}}$

Multiple-pulse effects exist.

$D_{ambi} \approx kT_e\mu_i / e$

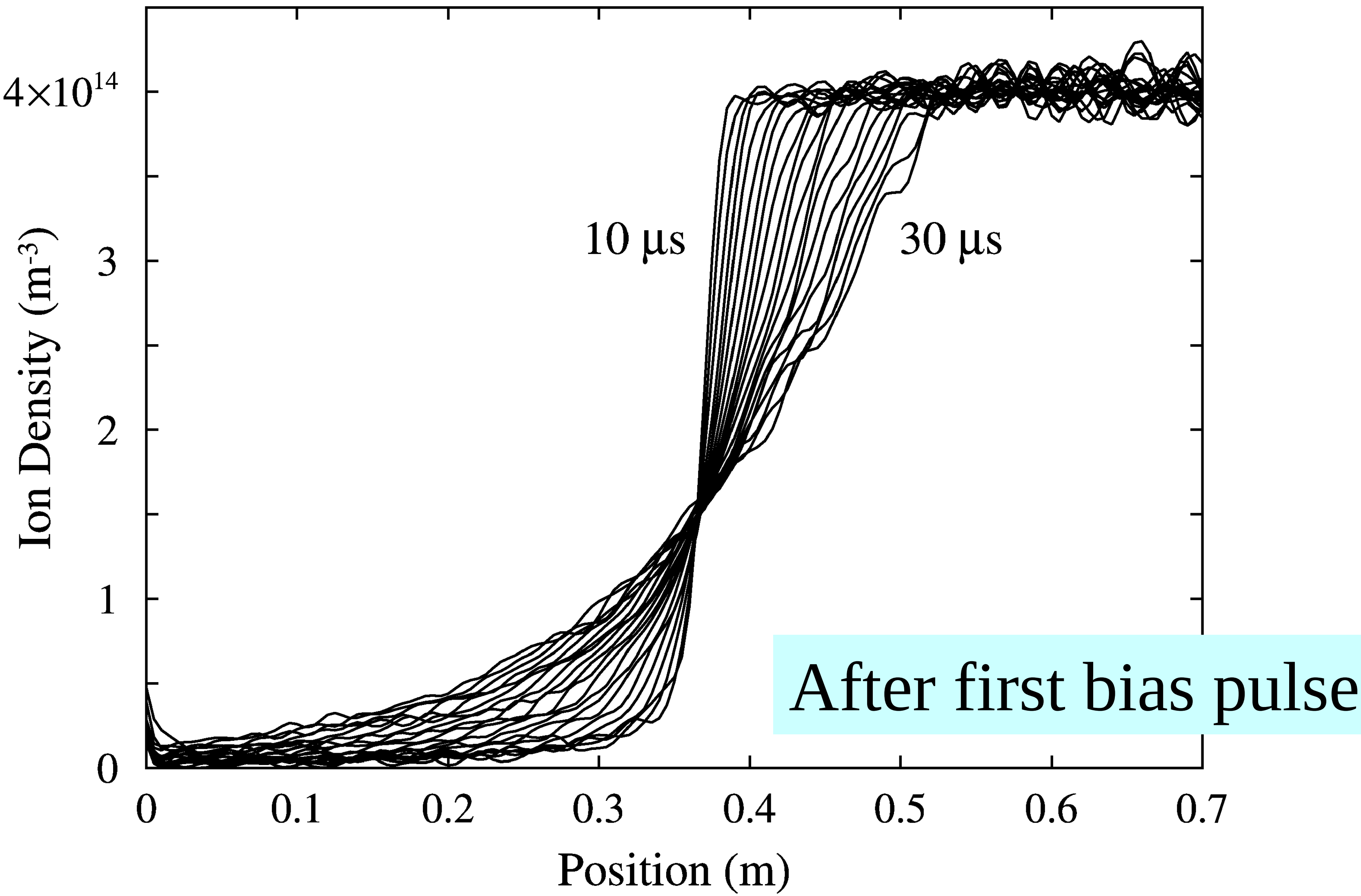
# Transient Sheath




First bias pulse

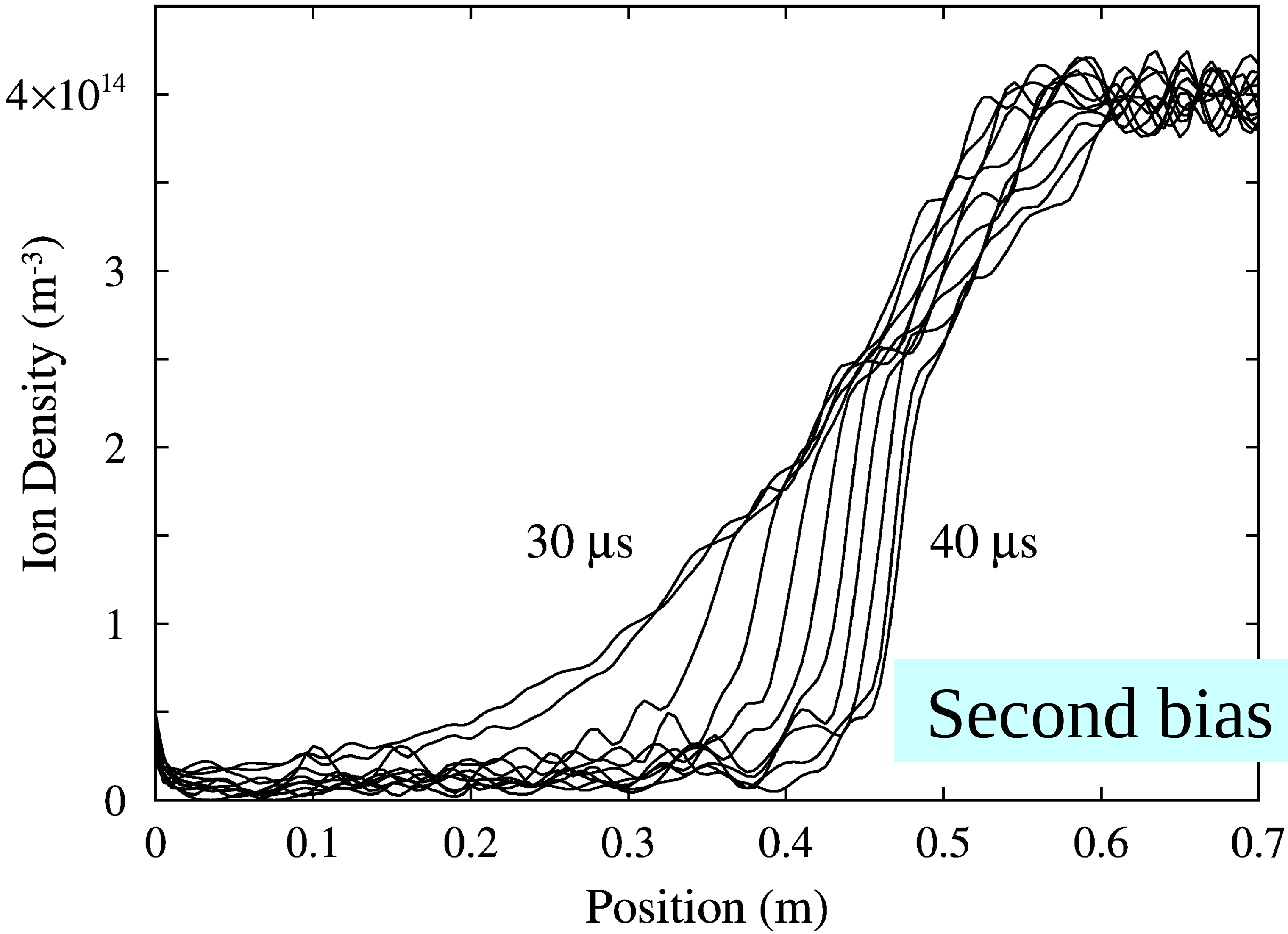
B. Wood, in: *Handbook of PIII&D*, Wiley, N.Y. 2000

# Transient Sheath




B. Wood, in: *Handbook of PIII&D*, Wiley, N.Y. 2000

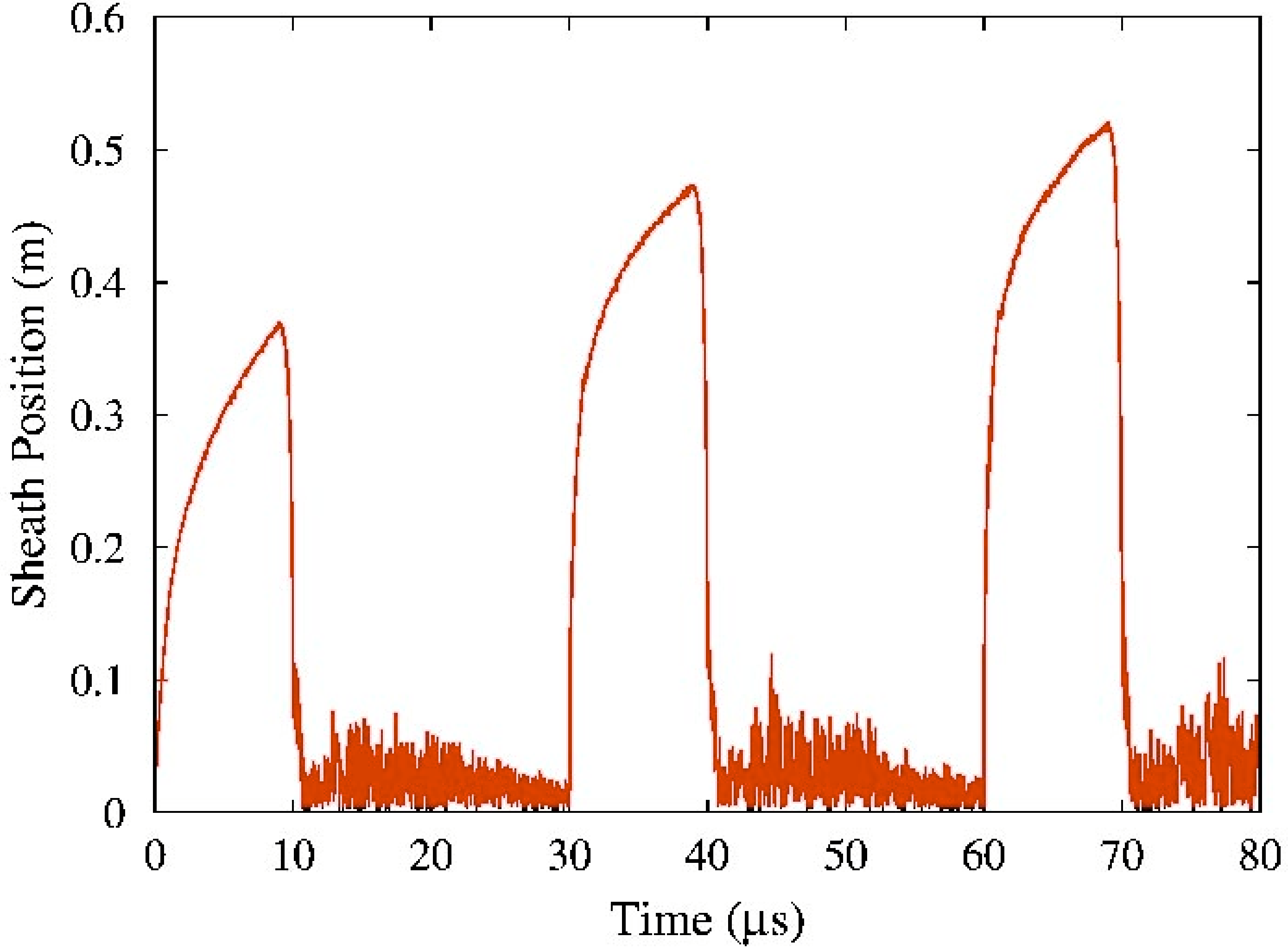
# Transient Sheath



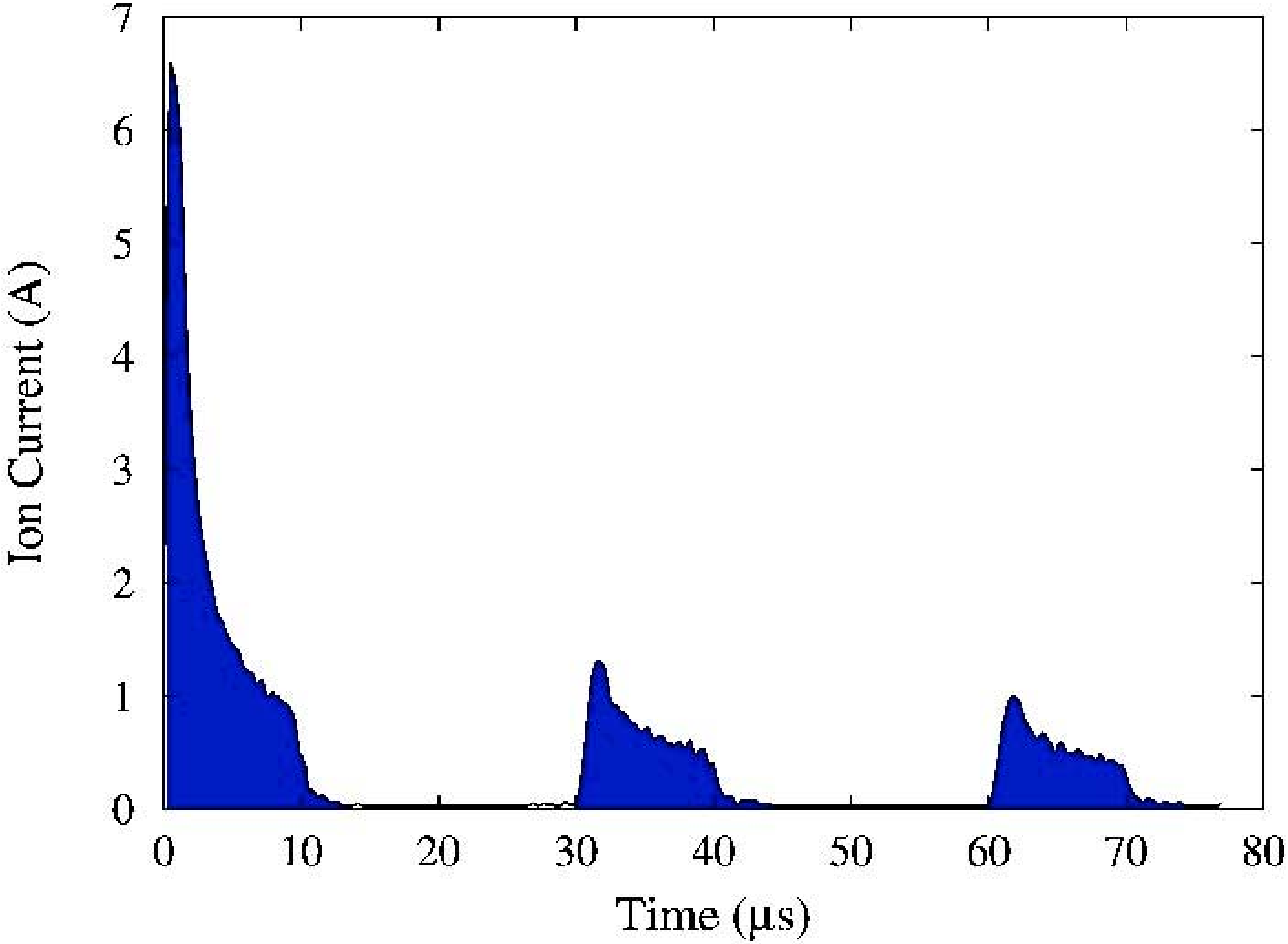

Second bias pulse

B. Wood, in: *Handbook of PIII&D*, Wiley, N.Y. 2000

# Multiple-Pulse Effects at High Duty Cycle



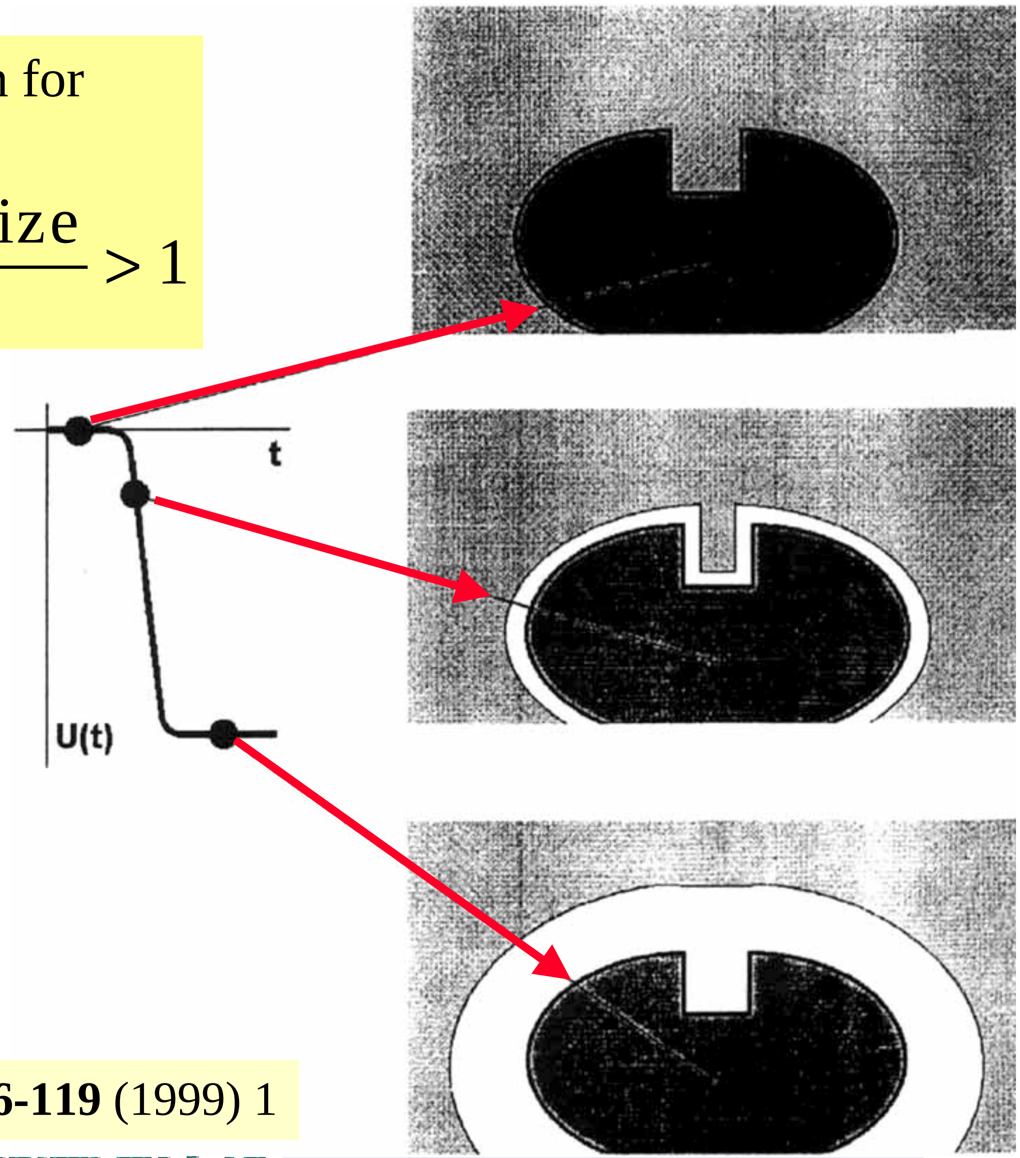
# Multiple-Pulse Effects at High Duty Cycle



# Dynamic Sheath

Dimensionless parameter as condition for conformal ion treatment:

$$\Lambda = \frac{\text{characteristic feature size}}{\text{sheath thickness}} > 1$$



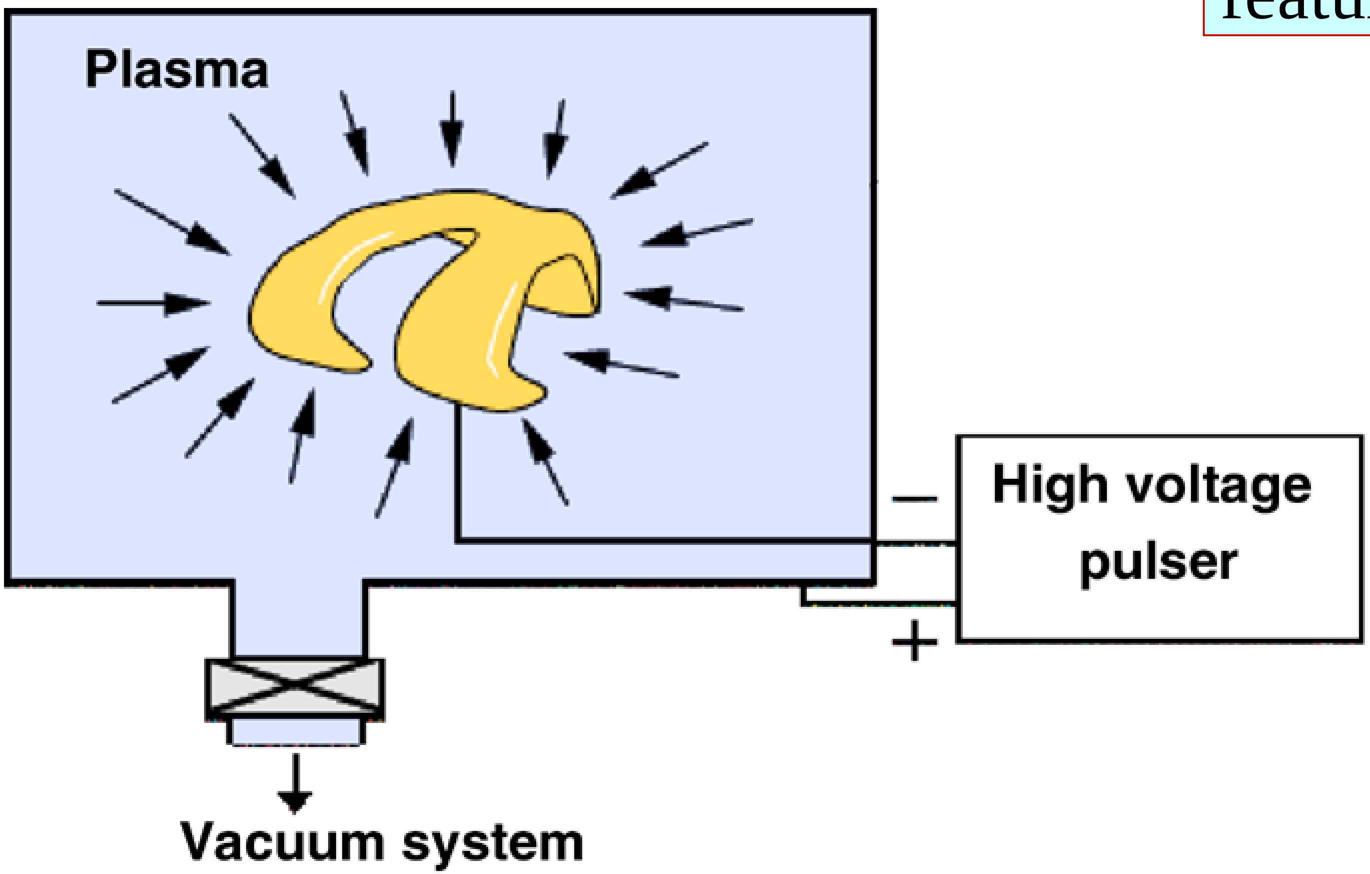

W. Möller, *et al.*, *Surf. Coat. Technol.* **116-119** (1999) 1

# Plasma Immersion Ion Processing

- PIIP - one kind of pulsed plasma CVD - proposed at LANL
  - M. Nastasi, et al., *Surf. Coat. Technol.* **136** (2001) 162
  - K.C. Walter, et al., *Surf. Coat. Technol.* **156** (2002) 306
- Plasma Immersion Technique with
  - carbon-containing gases (e.g. $C_2H_2$) for DLC films
  - organo-metallic precursor gases for e.g. metal carbo-nitride films
- pulsed sheath is utilized
  - to attract ions from plasma for energetic condensation AND
  - to accelerate secondary electrons for plasma generation

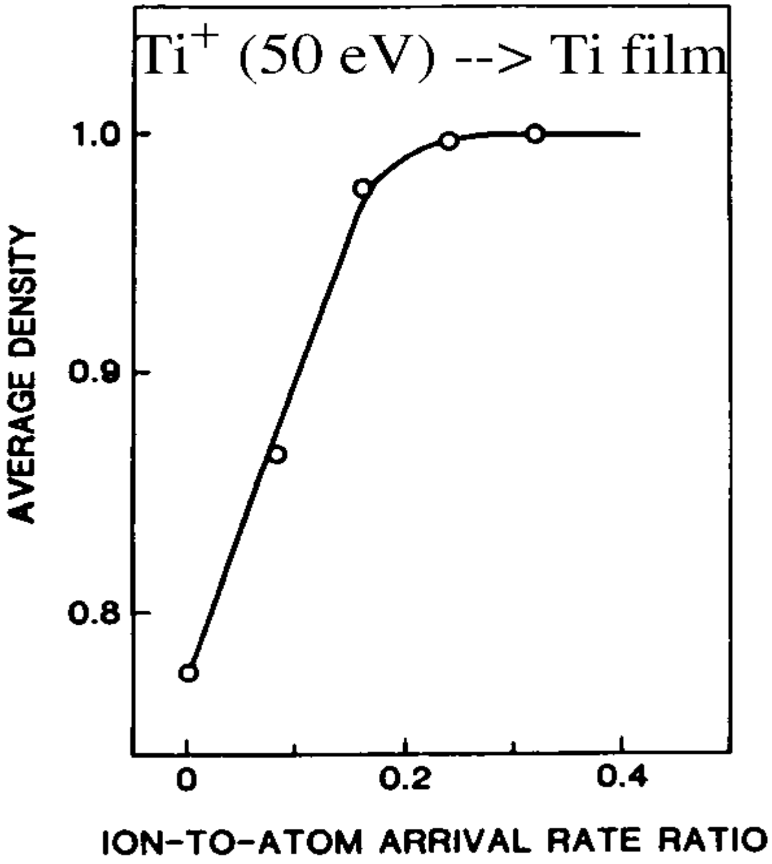
# Plasma Immersion Ion Processing

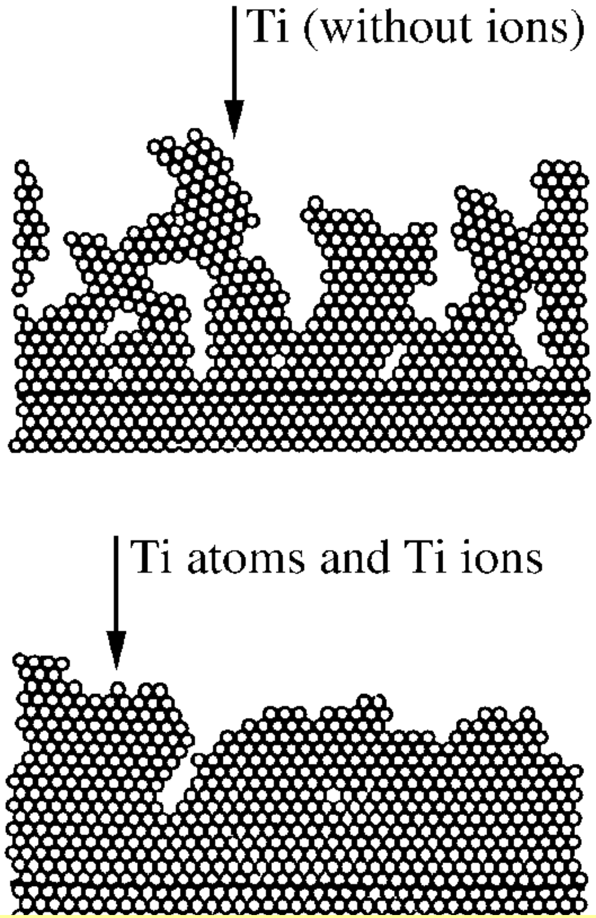
- designed for 3-dim coatings
- however, uniformity / conformal treatment only if $\frac{\text{sheath size}}{\text{feature size}} < 1$



# Effect of self-ion bombardment on film microstructure

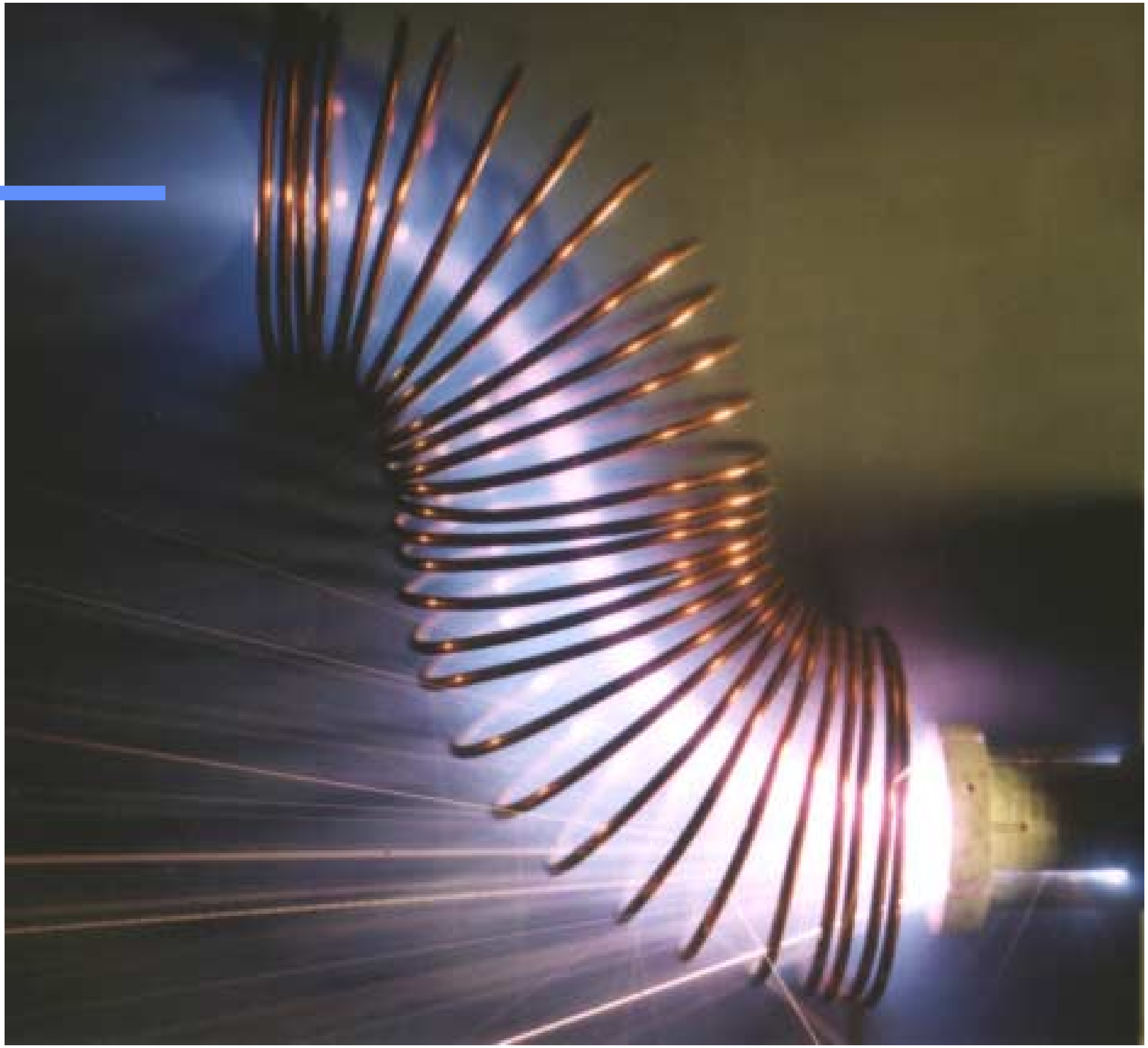
- Densification of Ti film by Ti ions (self-ion assistance)
- MC computer simulation (1987)




Martin et al. *JVST* **5** (1987) 22

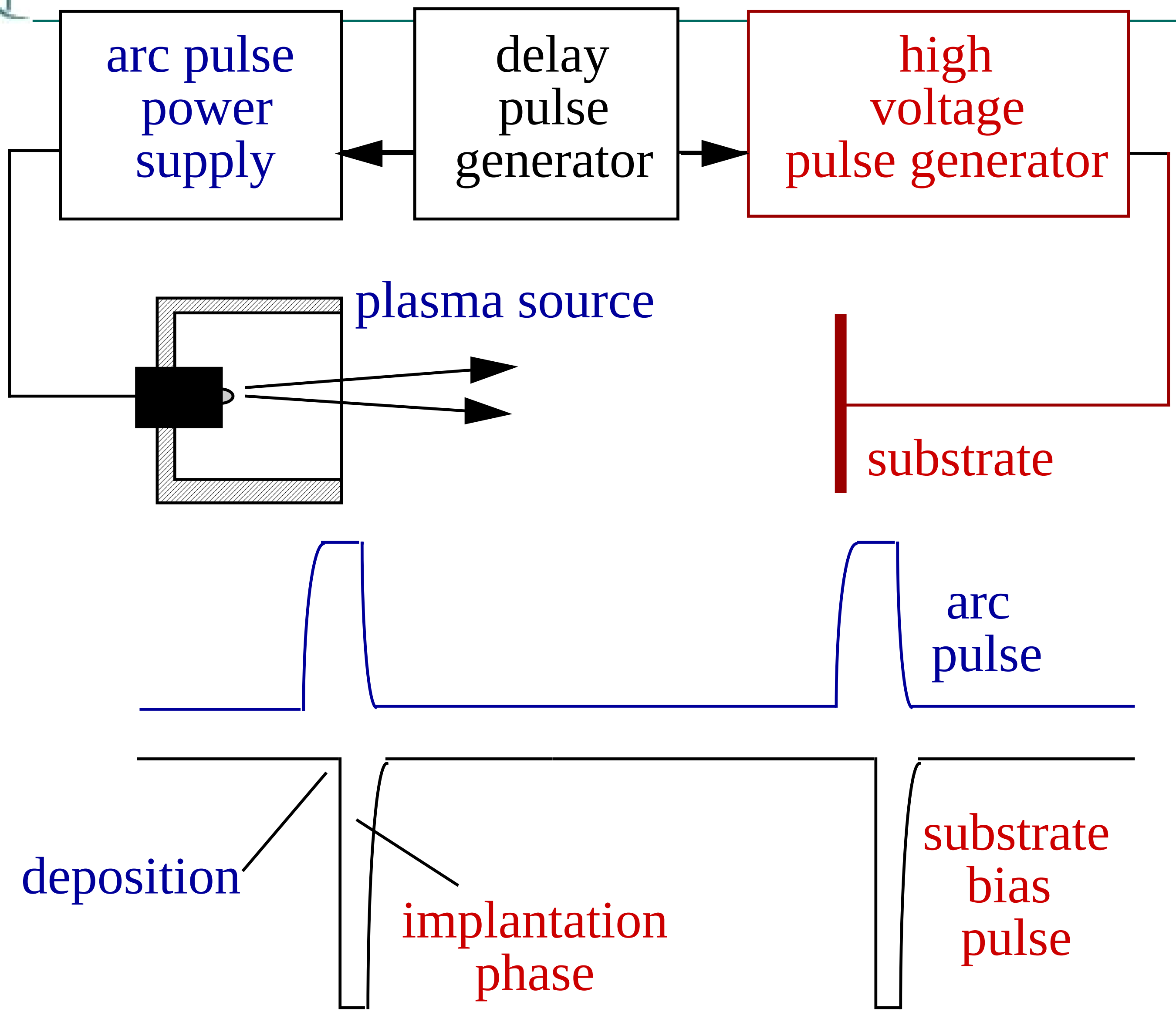
# Pulsed Filtered Cathodic Arcs



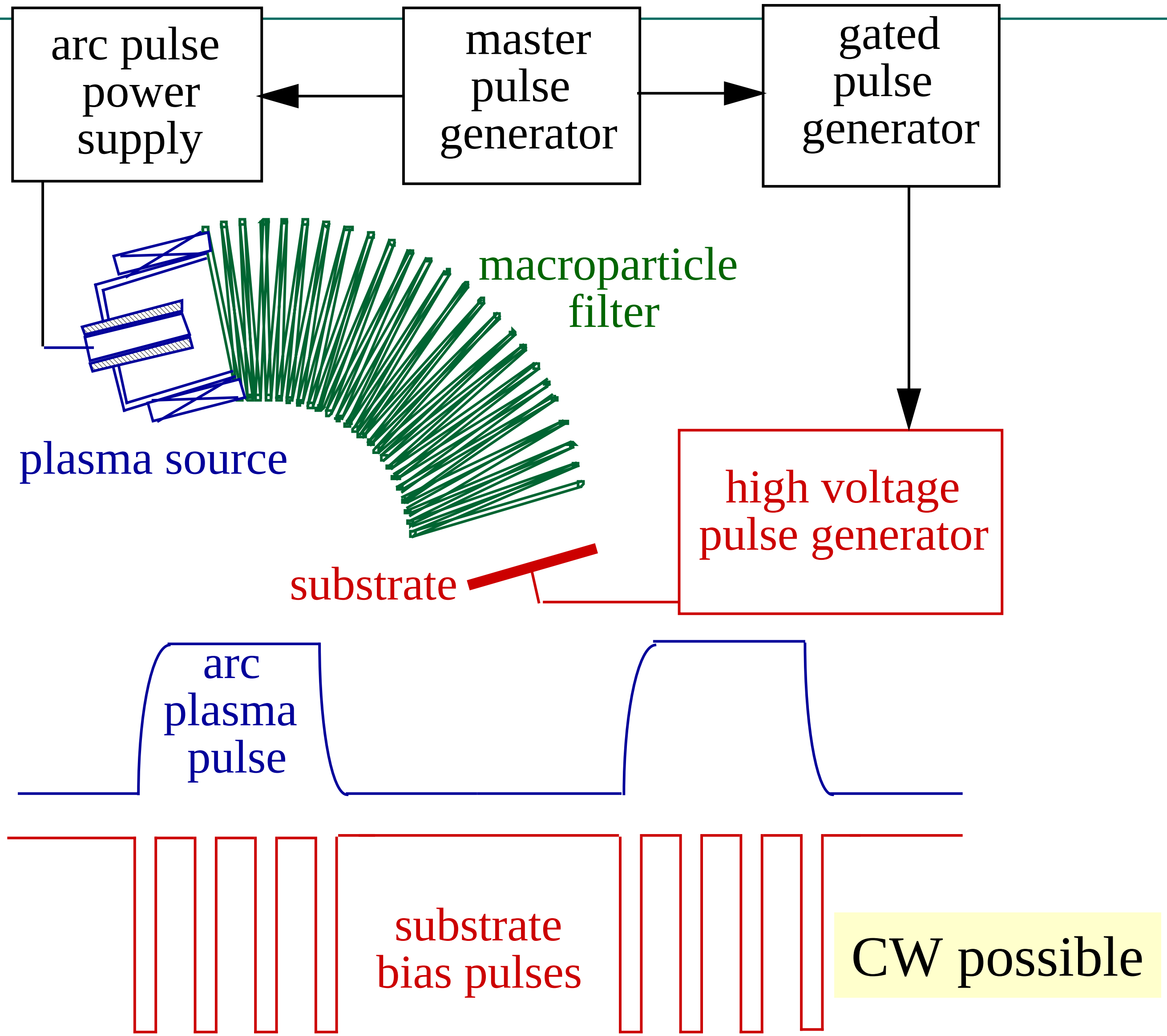
- clean metal plasma

- ta-C
- metal films
- compounds

# MePIIID

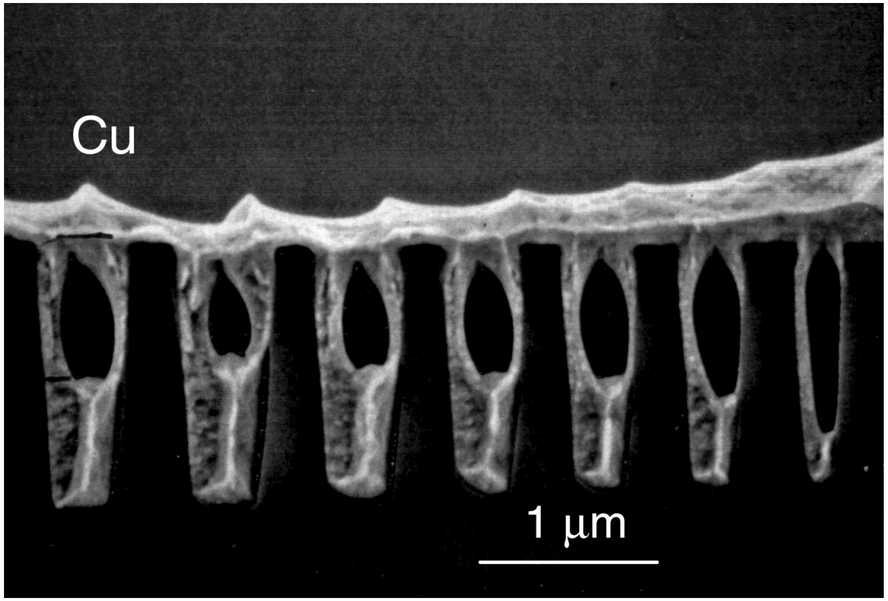

arc pulse power supply
delay pulse generator
high voltage pulse generator
plasma source
substrate
arc pulse
substrate bias pulse
deposition
implantation phase

# MePIIID

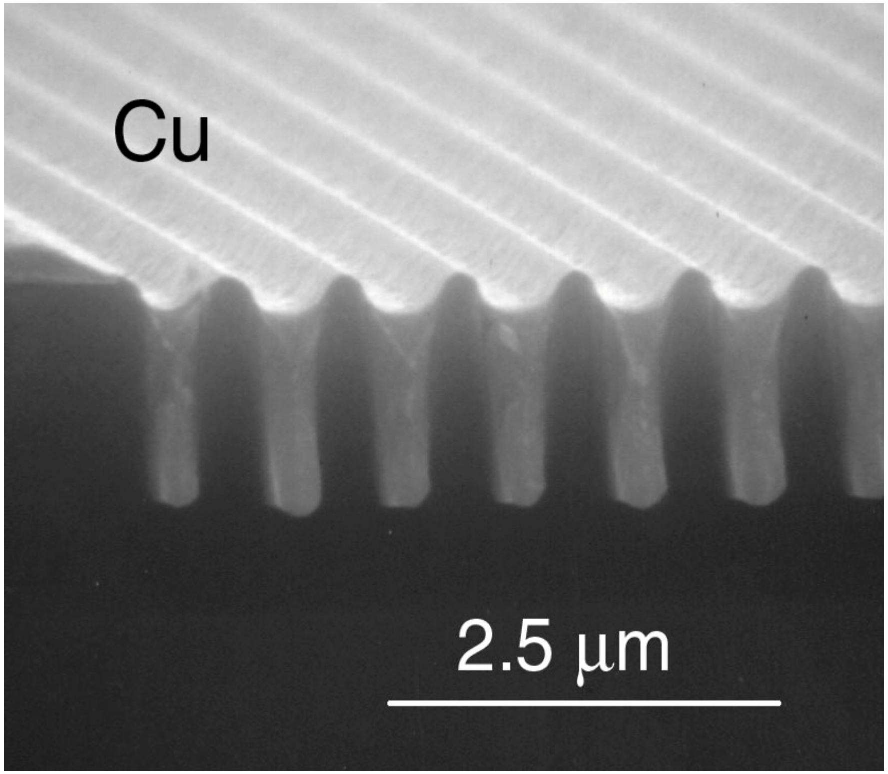

arc pulse power supply
master pulse generator
gated pulse generator
macroparticle filter
plasma source
high voltage pulse generator
substrate
arc plasma pulse
substrate bias pulses
CW possible

# Metallization by MePIIID

Copper metallization of sub-μm trenches and vias




voids form if vapor / plasma does not have correct impact angle and energy

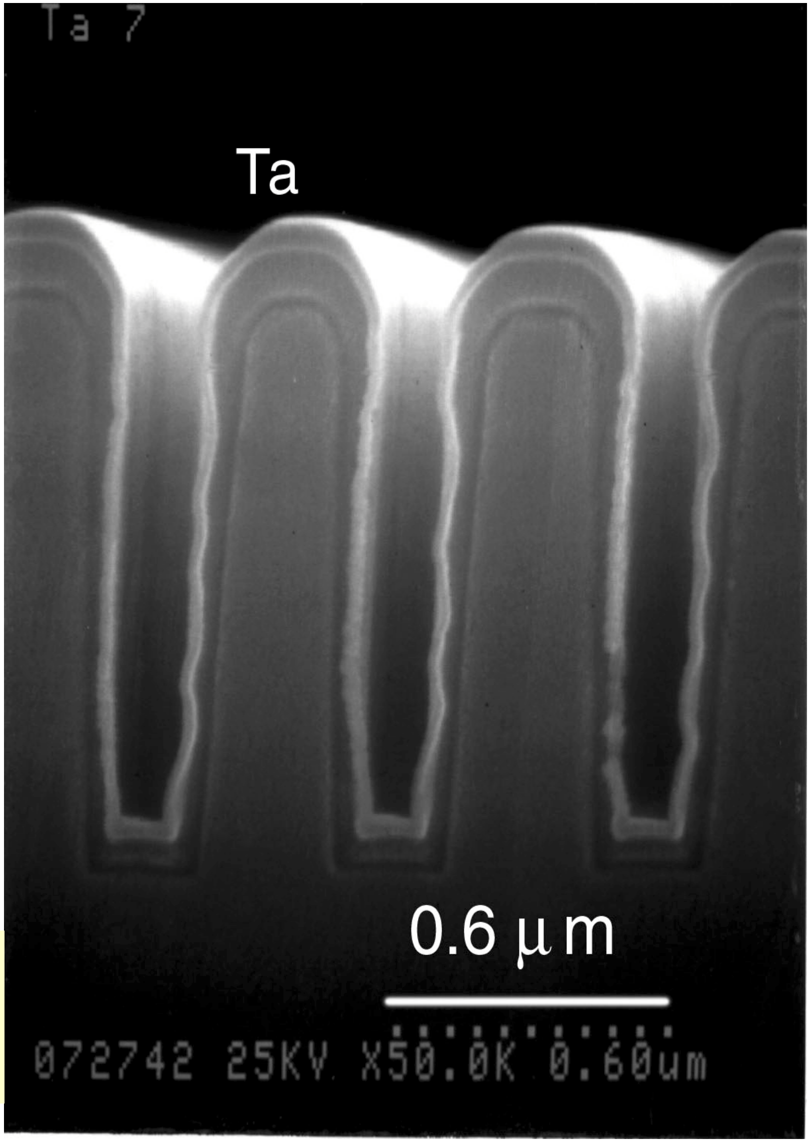



perfect filling of trenches

O.R. Monteiro, J. Vac. Sci. Technol. B **17** (1999) 1094

# Diffusion Barriers by MePIIID

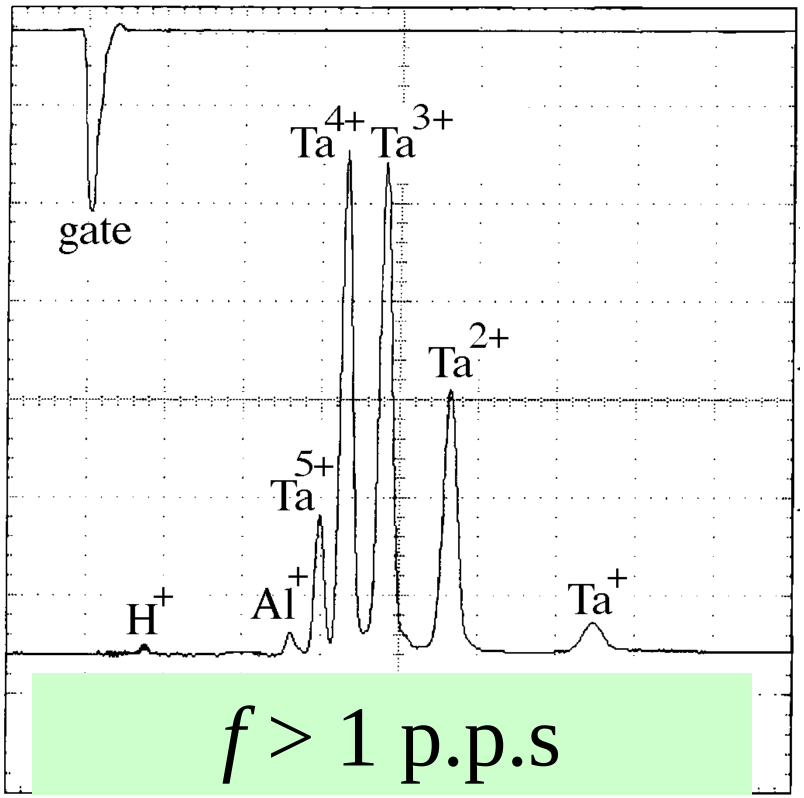
- Copper diffuses in silicon, hence need for diffusion barrier
- Ta and TaN can serve as barrier
- can be deposited conformally using MePIIID

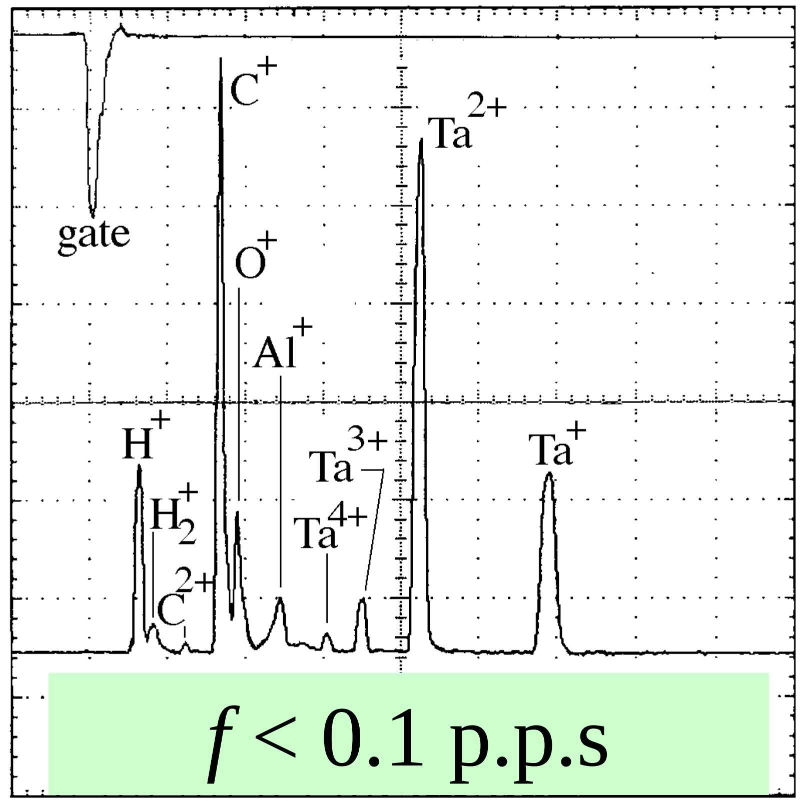



O.R. Monteiro, J. Vac. Sci. Technol. B **17** (1999) 1094

# Initial Plasma Composition

- Plasma can be significantly contaminated at beginning of each pulse, example: Ta arc, 250 μs

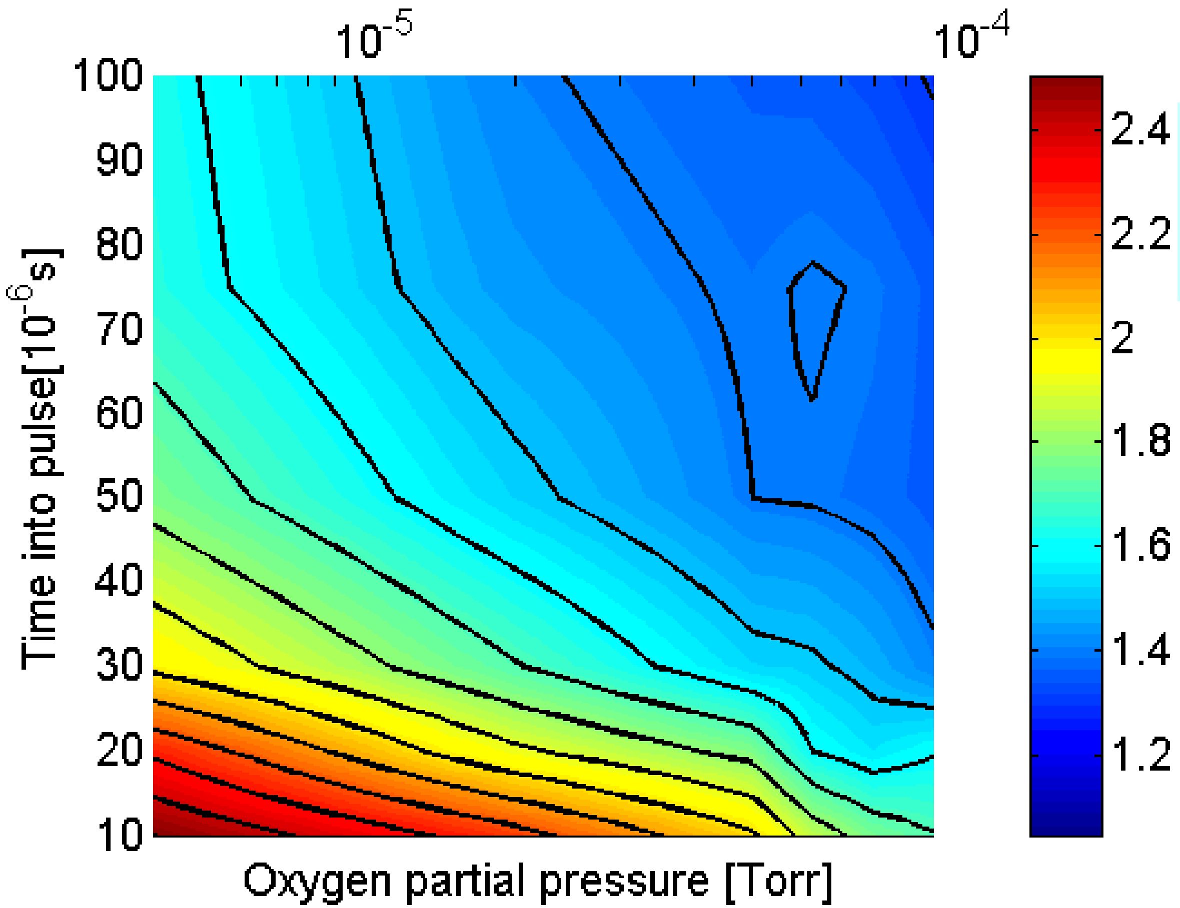



G.Yu. Yushkov et al., *IEEE Trans. Plasma Sci.* **26** (1998) 220.

# Temporal Development of Plasmas

## Example: Al plasma in oxygen background gas

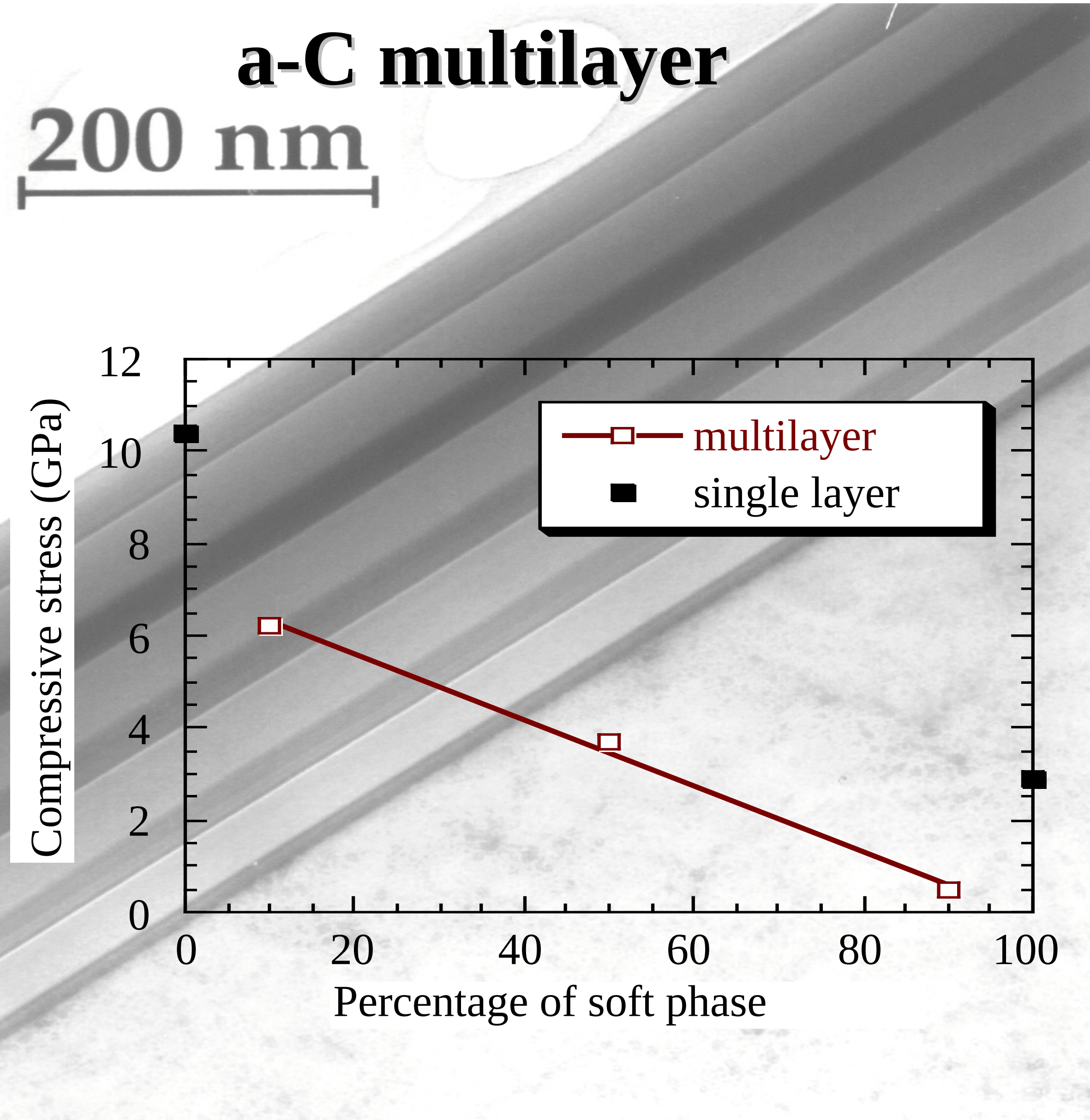



Mean ion charge state

J. M. Schneider, et al., Appl. Phys. Lett. **75**, (1999) 612.

# Effect of self-ion bombardment on film microstructure

- Si substrate, PIII intermixed layer
  (C, 2.2 keV
  2μs on/6 μs off)
- “hard” a-C / “superhard” a-C
  (4 double layers, with 2200 eV and 100 eV, each)

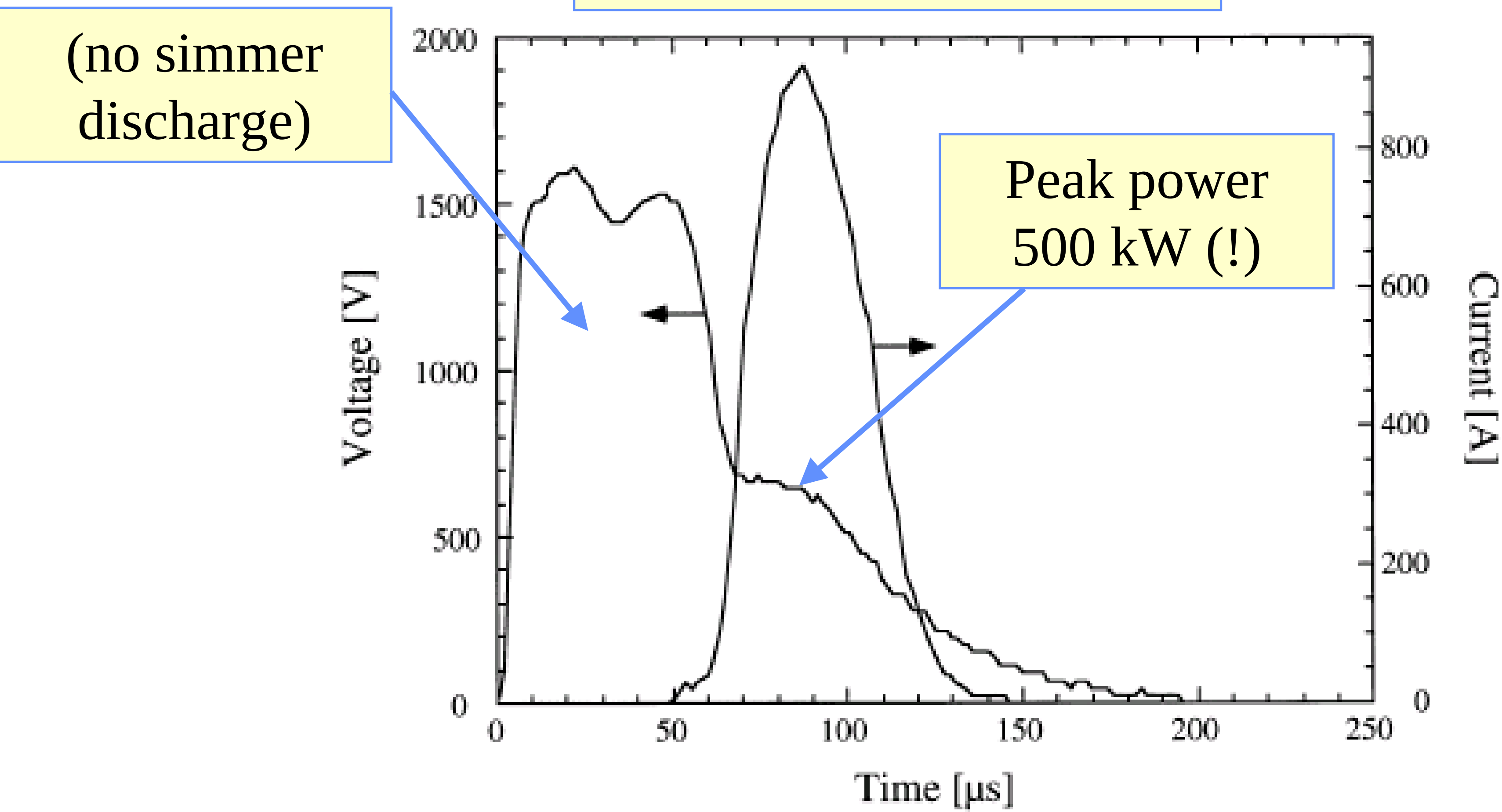


# Pulsed Sputtering

- Proposed by Kouznetsov and co-workers in late 1990s
- use of traditional sputter magnetron
- increase power during pulses by > 2 orders of magnitude
- average power is within acceptable level by using low duty cycle
- observe increased degree of ionization

# Voltage-Current Waveform for Pulsed Sputtering

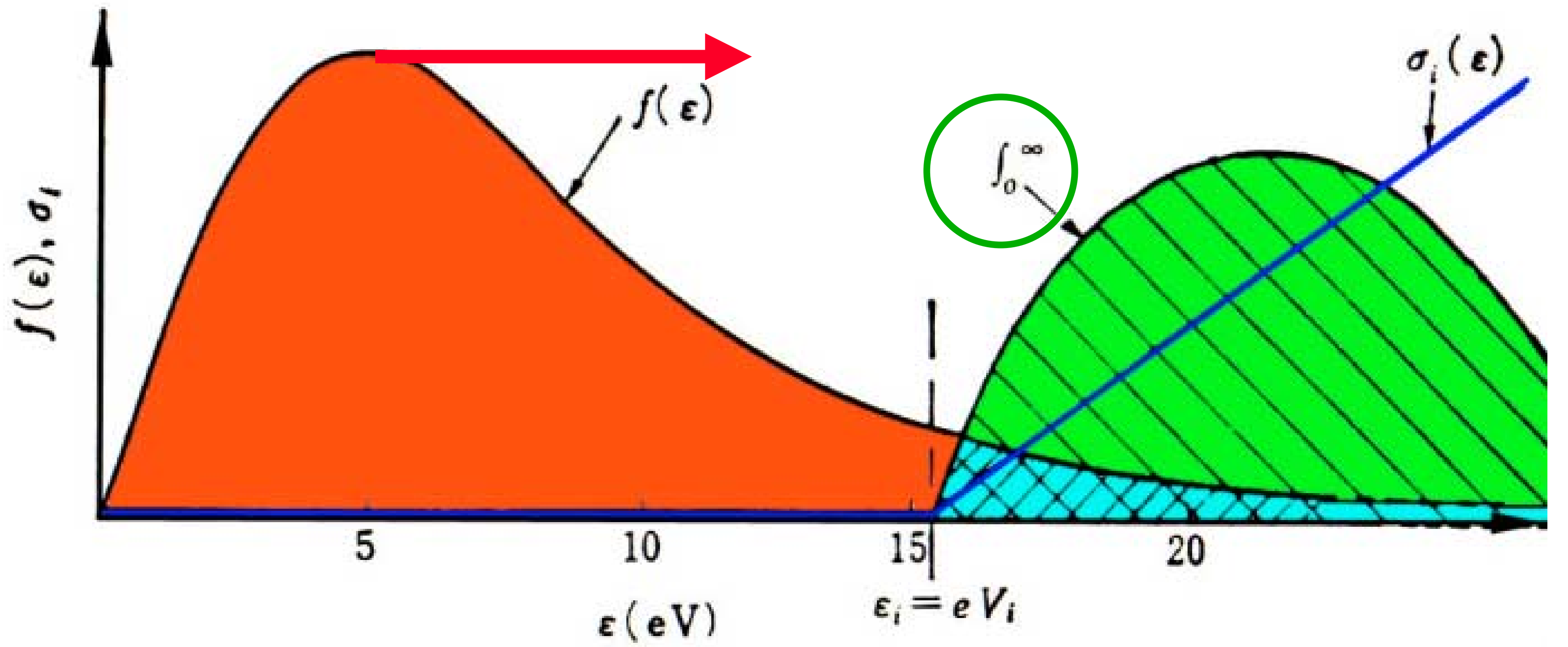
Cu target, 65 mPa Ar



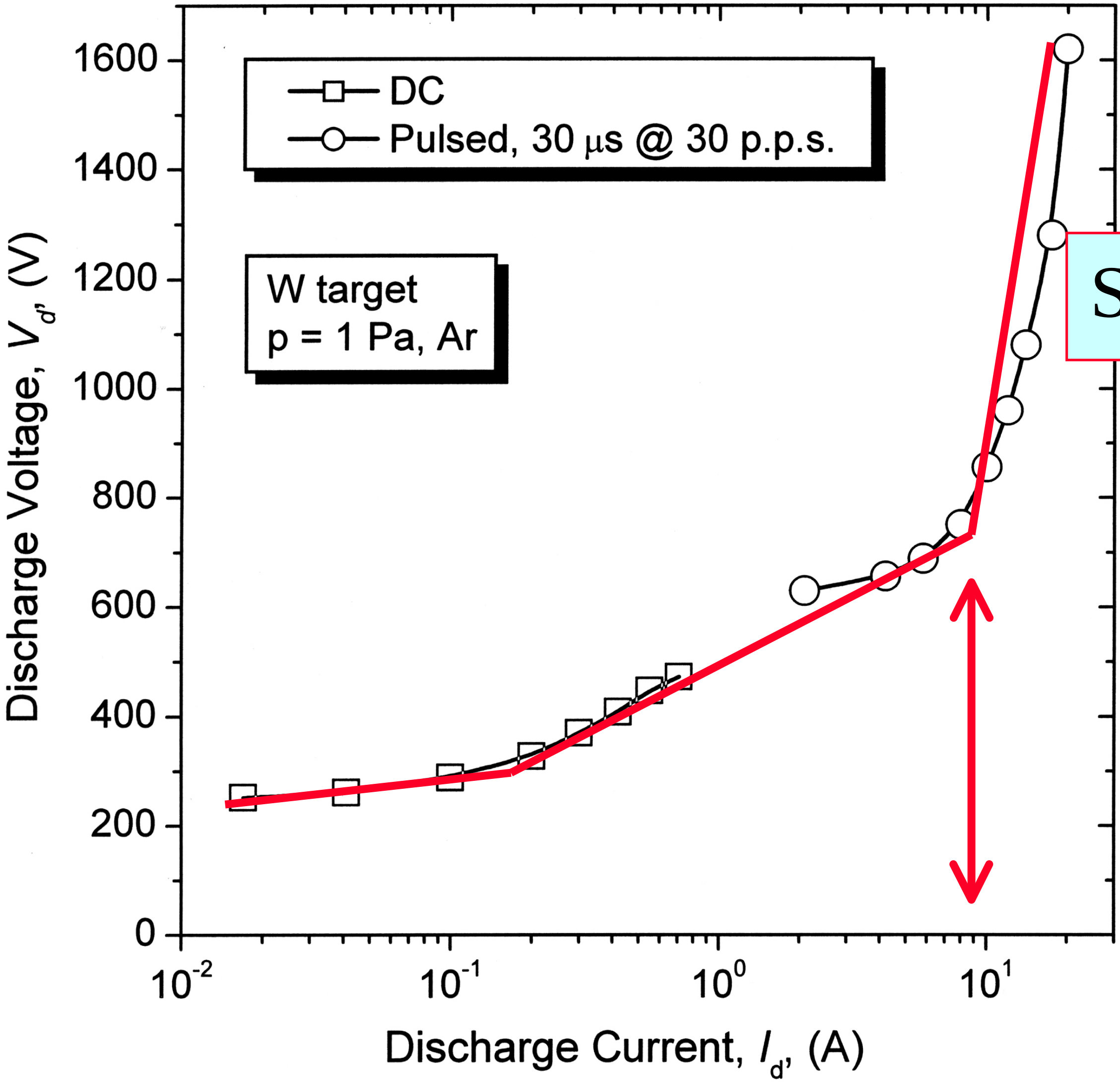

From: V. Kouznetsov, et al., *Surf. Coat. Technol.* **122**, 290-293 (1999).

# Distribution Functions and Rate Coefficients

Mean free path $\lambda_\alpha = \left( \sum_\beta n_\beta \sigma_{\alpha\beta} \right)^{-1}$



# V-I Characteristics of a Magnetron Discharge




$$I_d = cV_d^q$$

Slope $q \rightarrow 1$

A similar result was obtained for **Cr**, see: A.P. Ehiasarian, et al., *Vacuum* **65**, 147 (2002).

# Physics of Pulsed Sputtering

❑ Transition in characteristics:

High power density

partially ionized plasma → fully ionized plasma

gas-species dominated plasma → metal-species dominated plasma

# Physics of Pulsed Sputtering

Knudsen number for ionization $\mathrm{Kn} = \lambda_{ion} / \ell \ll 1$

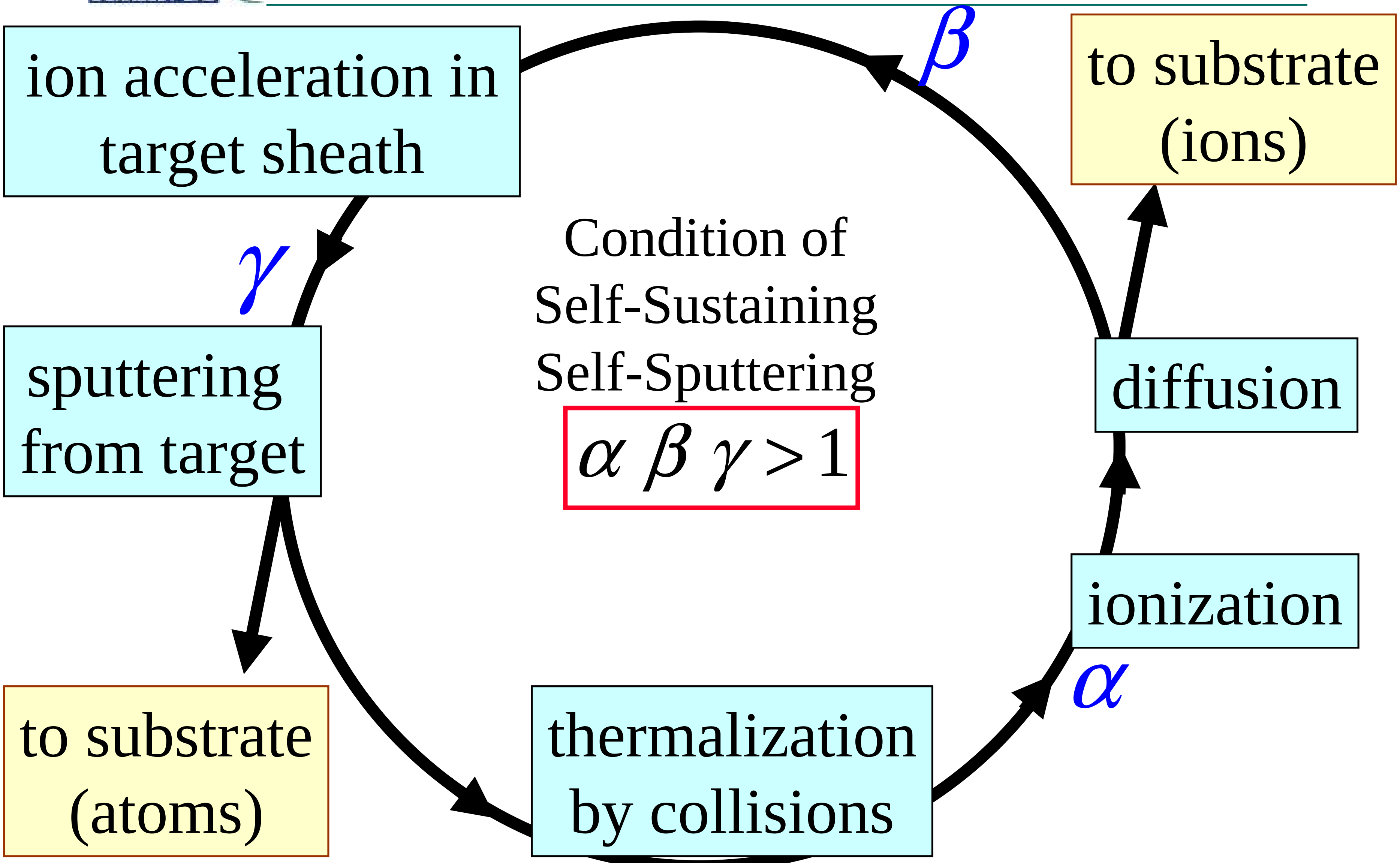
- thermalization
- ionization

- If there was no thermalization of sputtered atoms with background gas $u_{a0} = \sqrt{2E_{a0}/m_a} \sim 1000 \text{ m/s}$

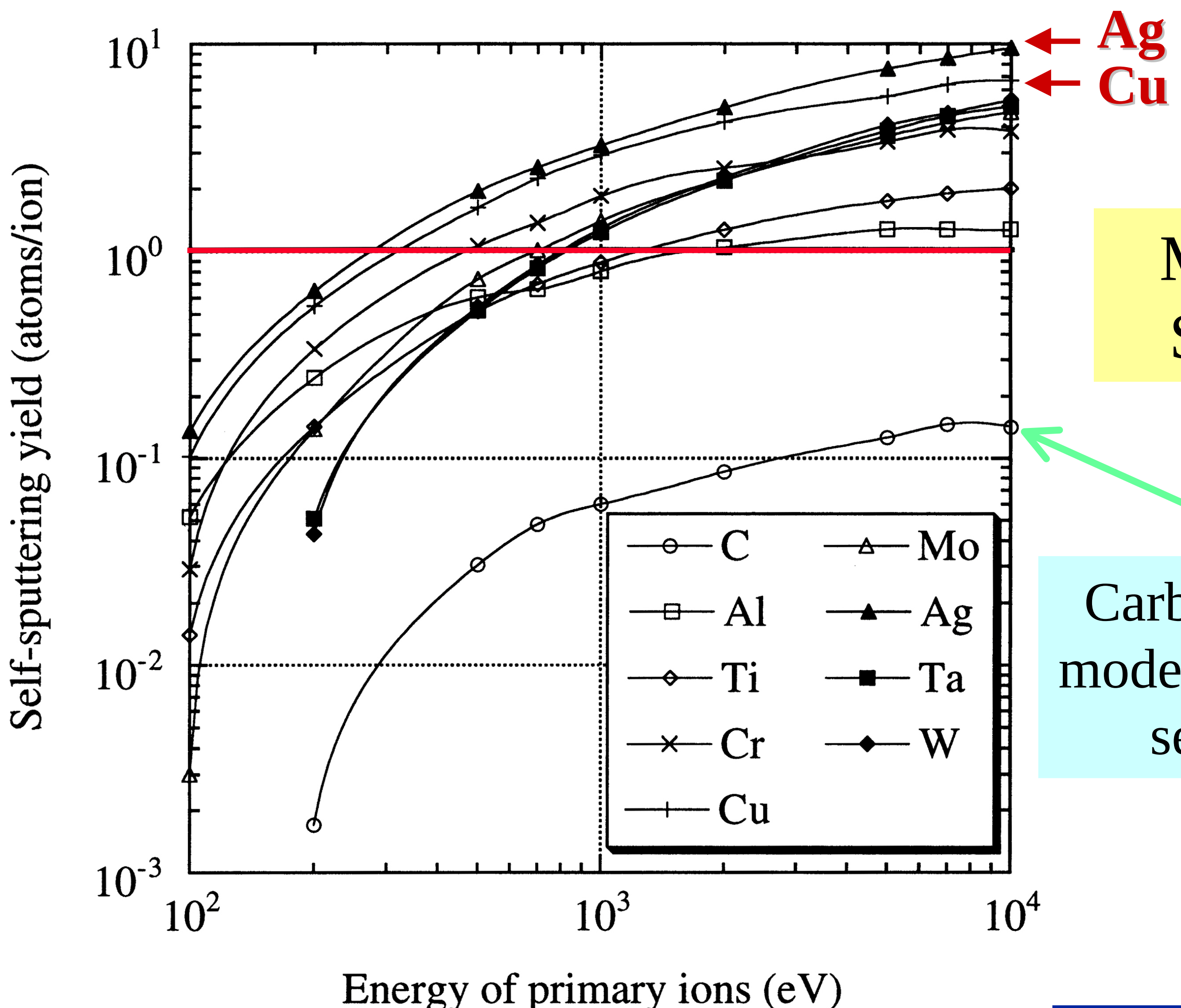
- thermalized and ionized atoms may return to target:

Self-sputtering

# Self-Sustained Self-Sputtering



# Self-Sputter Yield




Monte Carlo Simulations

Carbon cannot go in mode of self-sustained self-sputtering

# Summary / Conclusions

- Pulsed plasma processing
  - high kinetic energy in allows films growth to occur much further from thermodynamic equilibrium than with continuous processing
  - extreme pulsed plasma parameters can be reached
  - new process "control knobs" appear, such as duty cycle and pulse duration
- Many examples
  - here in detail: emerging technology of pulsed sputtering
  - for many materials: pulsed sputtering may lead to the mode of pulsed, self-sustained self-sputtering